Louisiana State University
LSU Digital Commons

LSU Historical Dissertations and Theses | Graduate School

1971

Reactions of Activated Olefins and Acetylenes With Hydridoiridium Complexes.

Margaret Shirley Fraser
Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation
Fraser, Margaret Shirley, "Reactions of Activated Olefins and Acetylenes With Hydridoiridium Complexes." (1971). *LSU Historical Dissertations and Theses*. 2050.
https://digitalcommons.lsu.edu/gradschool_disstheses/2050

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.

72-3486

FRASER, Margaret Shirley, 1925-
REACTIONS OF ACTIVATED OLEFINS AND ACETYLENES WITH HYDRIDOIRIDIUM COMPLEXES.

The Louisiana State University and Agricultural and Mechanical College, Ph.D., 1971
Chemistry, inorganic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

REACTIONS OF ACTIVATED OLEFINS AND ACETYLENES WITH HYDRIDOIRIDIUM COMPLEXES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Margaret Shirley Fraser
B.S., University of Alberta, Canada, 1948
M.S., University of Alberta, Canada, 1950
August, 1971

PLEASE NOTE:

Some Pages have indistinct print. Filmed as received.

UNIVERSITY MICROFILMS

ACKNOWLEDGMENT

The author wishes to express gratitude to the director of this research, Professor W. H. Baddley. His enthusiastic interest and encouragement throughout this work are sincerely appreciated. Acknowledgment is also made to other members of the Chemistry faculty and staff who have been of assistance. Sincere appreciation is extended to Professor Robert V. Nauman, Director of the Institute for College Chemistry Teachers.

Financial assistance from the National Science Foundation during attendance at Summer Institutes for College Teachers of Chemistry and in the form of a twelve month Faculty Fellowship is gratefully acknowledged. Some support from the Dr. Charles E. Coates Memorial Fund of the Louisiana State University Foundation for expenses pertinent to the publication of the doctoral dissertation is acknowledged.

LIST OF ABBREVIATIONS

Et_3P	triethylphosphine
Ph_3P	triphenylphosphine
Ph_3As	triphenylarsine
HCBD	hexachlorobutadiene
THF	tetrahydrofuran
TCNE	tetracyanoethylene
MeOH	methanol
EtOH	ethanol
PhC≡CH	phenylacetylene
PhC≡CPh	diphenylacetylene

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The reactions of various activated olefins with one or more of the iridium substrates, $IrH(CO)(Ph_3P)_3$, $IrH(CO)_2(Ph_3P)_2$ and $IrH_3(CO)(Ph_3P)_2$ have resulted in the formation of complexes of the type $IrH(CO)(\text{activated olefin})(Ph_3P)_2$ (activated olefin = fumaronitrile, cinnamonitrile, benzylidenemalononitrile and fumaric acid). Infrared, nmr and deuteration studies have led to the elucidation of the structures of these hydrido-olefin complexes. Nmr evidence suggests that fumaronitrile is rigidly bonded to the iridium in a "metallacyclopropane" ring structure.

The activated olefins, cinnamic and maleic acids, do not form π-olefin complexes, but rather protonate the iridium substrates used. The nmr spectra of these protonated species have been obtained, and the results corroborate the structures previously proposed on the basis of infrared studies.

A number of olefin complexes have been prepared from $IrCl(CO)(Ph_3As)_2$ in order to compare the relative stabilities of these with the corresponding olefin complexes of $IrCl(CO)(Ph_3P)_2$, and with the hydrido-olefin complexes. The electron-releasing properties of the hydrido-ligand and the Ph_3As ligand tend to increase the stability of the olefin-complex.

Tetracyanoethylene forms a σ-keteniminato-π-olefin complex with the iridium substrates, and several possible mechanisms for the reactions have been proposed. A by-product which forms in this reaction if alcohol is present has been formulated as $Ir(CN)(CO)(Ph_3P)_2$.

A σ-keteniminato-π-olefin complex has been assigned to the product of the reaction between benzylidenemalononitrile and $IrH(CO)_2(Ph_3P)_2$, but further study on this complex is required.

The activated olefin, acrylonitrile, produces a σ-cyanoethyl-π-olefin complex from $IrH(CO)(Ph_3P)_3$. The π-bonded moiety can be replaced by fumaronitrile.

The reactions of phenylacetylene with $IrH(CO)_2(Ph_3P)_2$ and with $IrH(CO)(Ph_3P)_3$ to produce $IrH(C{\equiv}CPh)_2(CO)(Ph_3P)_2$ were compared, and a rationale is presented to explain the slow reaction of the acetylene with the latter iridium substrate. The disubstituted acetylene, hexafluorobutyne-2, reacts similarly with both iridium substrates to produce a σ-vinyl-π-acetylene complex. Diphenylacetylene reacts with $IrH(CO)_2(Ph_3P)_2$ to give a yellow crystalline product, but no formulation has been assigned to this complex.

INTRODUCTION

The concept of a distinct class of transition metal hydride complexes began with Wilkinson's discovery in 1955 of $(C_5H_5)_2ReH$.[1] Although the first reasonably well defined, but unstable, hydride complexes of transition metals, $FeH_2(CO)_4$ and $CoH(CO)_4$,[2] were known in the early 1930's, the mode of bonding of the hydrogen in these and related compounds was not well understood. Wilkinson's study of $(C_5H_5)_2ReH$ by nuclear magnetic resonance techniques revealed that the resonance of a hydrogen nucleus attached to a transition metal atom shows an exceptionally large high field chemical shift as compared with hydrogen bound to the main group metals. For example, the proton chemical shifts for some Sn and Ge hydrides range from 2 to 5 ppm relative to tetramethylsilane,[3] whereas for the hydrido-complexes of the transition metals they generally range from -10 to -25 ppm.[4]

This diagnostic property for a proton linked to a transition metal made possible the detection of unstable transition metal hydrides which are formed in solution but whose isolation is either difficult or impossible. For instance, in the strongly reducing solution of $CoCl_2$ containing KCN, the presence of $[CoH(CN)_5]^{-3}$ had been inferred, but only recently was it detected by nmr.[5] Final proof of its existence came when the salt, $K_3CoH(CN)_5$, was isolated.[6]

Another characteristic property[7] which has been used in detecting the presence of a transition metal-hydrogen bond is the infrared M-H stretching frequency, ν_{M-H}, generally observed in the

range 2200-1700 cm^{-1}. The M-H bending mode, δ_{M-H}, occurs in the range 950-700 cm^{-1}, but strong bands due to other ligands frequently obscure this spectral region.

The realization that hydrogen can occupy a site in the coordination shell around the central metal atom helped clarify much of the early work on carbonyl hydrides and gave impetus to the search for other hydrido-complexes. Today, the known hydrido-complexes number in the hundreds, and reviews on this area have been published.[4,7]

Hydrido-complexes of the transition metals have the general formula $[M_xH_yL_z]$, where M is a transition metal to which the hydrogen and L, the ligand, are directly attached. The most common ligands are carbon monoxide, the π-cyclopentadienyl group, and tertiary phosphines, although halide and similar ions also occur with these, especially in the phosphine and phosphine carbonyl complexes.

The nature of the hydrogen varies considerably and tends to be protic in those complexes which contain two or more carbon monoxide molecules. The most striking example is $CoH(CO)_4$, said to be as strongly acid as nitric acid in methanol solution.[2] Dipole moment studies of some tertiary phosphine hydrido-complexes have been interpreted on the basis of the hydrogen carrying a small negative charge, consistent with the anionic character of the hydride in these types of complexes.[8]

According to Chatt,[8] the stability of the hydrido-complexes is due mainly to the total ligand-field stabilization energy of the ligands in the complex. The π-acid character of the ligands results

in an energy separation between the occupied non-bonding d-orbital energy levels and the vacant anti-bonding levels large enough so that homolytic or heterolytic splitting of the metal-hydrogen bond is not favored. Thus, the stabilities of analogous hydrido-complexes of the transition metals generally increase in passing from the lighter to the heavier element in any group in the Periodic Table.

The research undertaken for this Dissertation involved the study of the reactions of activated olefins and acetylenes with hydridocarbonylphosphine and arsine complexes of iridium. In particular, the isolation of stable hydrido-olefin complexes was sought, and these were expected to be more stable for iridium than its lighter congeners.

Hydrido-olefin complexes have often been postulated as unstable intermediates in a variety of homogeneous catalytic reactions including isomerization, dimerization and polymerization, hydrogenation, and hydroformylation of olefins.[9] The reactions are presumed to proceed from this intermediate by insertion of the olefin into the M-H bond to give the σ-alkyl complex.[10] The subsequent steps then depend on the nature of the catalytic reaction. An example of the importance of hydrido-complexes may be seen in the catalytic cycle believed operating in the hydroformylation (OXO reaction) reaction involving $HCo(CO)_4$ as catalyst.[11]

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (1)$$

$$HCo(CO)_3 \xrightarrow{RCH=CH_2} \left[\begin{array}{c} RCH=CH_2 \\ \downarrow \\ H\text{-}Co(CO)_3 \end{array}\right] \longrightarrow RCH_2CH_2Co(CO)_3 \qquad (2)$$

$$RCH_2CH_2Co(CO)_3 \xrightarrow{CO} RCH_2CH_2Co(CO)_4 \longrightarrow RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_3 \qquad (3)$$

$$RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_3 \xrightarrow{H_2} RCH_2CH_2\overset{O}{\overset{\|}{C}}CoH_2(CO)_3 \longrightarrow RCH_2CH_2\overset{O}{\overset{\|}{C}}H + HCo(CO)_3 \quad (4)$$

Although the hydrido-alkene intermediate (shown bracketed in eq. 2) is not isolable, the existence of such complexes would give credence to such a mechanism. Therefore, the preparation of stable hydrido-olefin compounds which could serve as models for these intermediates would be of interest and their study might contribute to a better understanding of the nature of the catalyst or the catalytic process.

A survey of the literature reveals that few hydrido-olefin complexes have been prepared, and that these, for the most part, have not been well characterized. Robinson and Shaw[12] obtained a 70% yield of $[IrHCl_2(C_8H_{12})]_2$ by heating an ethanolic solution of choroiridic acid with cycloocta-1,5-diene for two hours. The ν_{Ir-H} shifted from 2261 to 1613 cm^{-1} for the corresponding deuterido-complex.

Schrauzer and Dewhirst[13] reported on an impure hydrido-olefin complex of approximate composition, $DquIrHCl_2$ (Dqu = duroquinone), obtained from refluxing $IrCl_3$ and duroquinone in ethanol for 3 hr. Clark and Tsang[14] allowed $PtHCl(Et_3P)_2$ to react with tetrafluoroethylene and obtained HF and the σ-fluorovinyl derivative, $PtCl(CF{=}CF_2)(Et_3P)_2$ as the main products. A small yield (8%) of a compound believed to be the π-olefin complex, $PtHCl(C_2F_4)(Et_3P)_2$, was isolated, and although the infrared spectrum suggested the presence of a Pt-H bond, no high field nmr signal could be observed. The corresponding deuterium analogue was

not prepared. This compound was later shown not to be a hydrido-complex but rather trans-$[PtCl(CO)(Et_3P)_2]BF_4$.[15]

In the study[16] of the catalytic isomerization of cycloocta-1,5-diene (1,5-COD) to the 1,3-isomer using $PtCl_2(Ph_3P)_2$ with $SnCl_2 \cdot 2H_2O$ as co-catalyst, Tayim and Bailar isolated $[\{PtH(SnCl_3)(Ph_3P)_2\}_2(1,5\text{-COD})]$ and inferred the presence of the Pt-H bond from the infrared spectral data. The synthesis of the same compound outside the catalytic scheme involved heating the diene with a mixture of trans-$[PtHCl(Ph_3P)_2]$ and $SnCl_2 \cdot 2H_2O$. In a following publication[16] concerning hydrogenation reactions, two other related hydrido-complexes were isolated and also synthesized for comparison purposes.

Singer and Wilkinson[17] studied the oxidative addition reactions of HCN, H_2S, and other acids with phosphine complexes of Ir(I) and Rh(I) in order to find a catalyst for the addition of weak acids such as HCN to unsaturated molecules. From $[MCl(diolefin)]_2$, (M = Rh or Ir and diolefin = cycloocta-1,5-diene or norbornadiene) and HCN they obtained $RhCl(diolefin)(HCN)_2$ and $IrHCl(CN)(COD)$. The former compound was poorly characterized and for neither compound were ν_{M-H} bands confirmed by deuteration studies. Hallman, et. al.,[18] obtained an impure tan complex of stoichiometry $RuHCl(C_7H_8)(Ph_3P)_2$ from a solution of $RuHCl(Ph_3P)_3$ containing excess norbornadiene. The product was cited as a "rare example of a hydrido-alkene complex." Lately, Uguagliati and Baddley[19] reported the preparation of $PtHCN[(NC)_2C=C(CN)_2](Et_3P)_2$ from $PtHCN(Et_3P)_2$ and tetracyanoethylene. The presence of a M-H band in this compound was confirmed by deuteration studies.

This last mentioned publication is one of a series devoted to the study of the bonding capabilities of cyanoolefins with transition metals. The suggestion that activated olefins,[20] especially cyanoolefins[21] could lead to the formation of stable transition metal-olefin complexes is understood in the context of the Dewar-Chatt-Duncanson[22] model for metal-olefin bonding. This bond is customarily described as consisting of two parts: (a) a σ-bond formed by overlap of the filled π-orbital of the olefin with a vacant metal orbital (olefin → M); and (b) a π-bond obtained through overlap of the vacant antibonding orbital of the olefin with a filled d-orbital of the metal (M → olefin). If the M → olefin π-bond is the more important factor in contributing to the stability of the metal-olefin bond, then electron-withdrawing substituents on the olefin will enhance this stability. A number of such cyanoolefin complexes with the coordinatively unsaturated d^8 complex $IrCl(CO)(Ph_3P)_2$ have been reported.[23] The complexes obtained may be viewed (vide infra) as oxidative addition to $IrCl(CO)(Ph_3P)_2$ by the olefin to give the coordinatively saturated d^6 iridium(III) adduct.

For this research, the use of certain activated olefins with the coordinatively saturated d^8 iridium substrates, $IrH(CO)(Ph_3P)_3$ and $IrH(CO)_2(PH_3P)_2$ and the coordinatively saturated d^6 complex $IrH_3(CO)(Ph_3P)_2$ has led to the isolation of hydrido-olefin complexes of general formula $IrH(CO)(olefin)(Ph_3P)_2$. The stabilities of these complexes are comparable to (or greater than) the stabilities of olefin complexes of the chloro-analogue, and the two following citations will serve to reveal the role that the hydride ligand probably plays in this stability.

Harrod, et. al.,[24] found that $IrH(CO)(Ph_3P)_3$ undergoes oxidative addition (with the loss of a Ph_3P molecule, the intermediate may be viewed as a coordinatively unsaturated d^8 species) reactions with triaryl and trialkylsilanes more readily than does $IrCl(CO)(Ph_3P)_2$. The authors state that these results are in accord with the currently held belief that oxidative additions are promoted by the presence of electron releasing ligands on the reactant complex,[25] hydrogen being more electron releasing than chloride. Clark, et. al.,[26] reported a stable complex is formed from $IrCl(CO)(MePh_2P)_2$ and the activated olefin, tetrafluoroethylene, but the complex formed from $IrCl(CO)(Ph_3P)_2$ dissociates in solution.[27] The methyldiphenylphosphine in the former compound is a better σ-donor but a weaker π-acceptor ligand than triphenylphosphine, and the resulting high electron density on the metal atom leads to the formation of more stable compounds.

The nature of the bonding of olefins and acetylenes to transition metals has been under discussion in the literature for many years. For olefins, the discussions center around two alternate configurations depicted as follows:

I II

Structure I represents the conventional metal-olefin bond as found in Zeise's salt, $K[PtCl_3(C_2H_4)]H_2O$, with the oxidation state

of the metal unchanged from the substrate from which it was derived, i.e., $K_2[PtCl_4]$. Although coordinated olefins have generally been depicted as rigidly attached to metal ions with the olefin bond perpendicular to the coordination plane in 4-coordinate planar complexes, there is some evidence that free rotation of the olefin is possible in solution. Cramer[28] presented nmr data to show that ethylene coordinated to rhodium(I) in the compound π-$C_5H_5Rh(C_2H_4)_2$ can rotate with the coordination bond as axis. Structure II implies that the olefin is bonded via two σ-bonds in a "metallacyclopropane" ring structure with the oxidation state of the metal increased by +2 units. The latter type of structure, for instance, was proposed[26] for $IrCl(CO)(C_2F_4)(MePh_2P)_2$ on the basis of the temperature invariant ^{19}F nmr which showed two complex multiplets indicating a doubly σ-bonded rigid structure which has two different fluorine environments. Other authors[27] have used nmr as a basis for choosing between the two extreme structures depicted above. Vaska[29] has assigned relative oxidation states to Ir in a series of olefin complexes of $IrCl(CO)(Ph_3P)_2$ based on the observed shifts for the carbonyl stretching frequency relative to that in $IrCl_2I(CO)(Ph_3P)_2$ where Ir was assigned an oxidation state of +3. The increase in the carbonyl stretching frequency, if assumed to arise from weaker back-donation of electron density from the metal, would then provide an assessment of the positive charge on the metal.[23] This view of gradations from one limiting structure to the other has its proponents[30] in the analogous case for acetylene bonding to metals. Baddley[23] has suggested viewing the bonding from the molecular orbital approach

where a "pure π-bond" would be equivalent to the valence-bond conception of two σ-bonds.

During the course of this work some nmr data pertinent to the above brief discussion was obtained and will be reported in the Results and Discussion section.

As mentioned previously, certain activated olefins gave rise to hydrido-olefin complexes. The reaction of tetracyanoethylene with the aforementioned iridium substrates produced a rather novel product containing a π-bonded tetracyanoethylene group and a σ-bonded ketenimine group.

Keteniminato-complexes of the transition metals are not unknown, but they are not common. Beck and coworkers[31] utilized potassium tricyanomethanide, $K(C_4N_3)$, to form complexes of general formula $M(NO_2)L(C_4N_3)$ ($M = Co, Ni$; $L = Ph_3P, (C_6H_{11})_3P$), from metal nitrosyl halides. In further studies,[32] compounds were formed from metal carbonyls according to the reaction given by eq. 5.

$$M(CO)_6 + K[C(CN)_3] \xrightarrow[120^\circ]{\text{diglyme}} K[M(CO)_5(C_4N_3)] + CO \qquad (5)$$

where M = Cr, Mo, or W.

Tetracyanoethylene, reacting with $(C_5H_5)Fe(CO)_2CH_2C_6H_5$ in dichloromethane at 25° for 9 hr, leads to 1,2- and 1,4-insertion of $(NC)_2C=C(CN)_2$ into the $Fe-CH_2C_6H_5$ bond.[33] The 1,4-insertion product

exhibits strong bands at 2151 cm^{-1} and 1296 cm^{-1} which were assigned to asymmetric and symmetric N=C=C stretches respectively.

Ketenimines are known for main group elements also. Neumann and coworkers[34,35] have prepared ketenimines of Sn and Pb by this general reaction:

$$R^1HC{=}C\begin{matrix}CN\\CN\end{matrix} + R_3MH \rightarrow R^1HC(H)\text{-}C(CN){=}C{=}N\text{-}MR_3 \qquad (6)$$

R^1 = e.g., CH_3, C_6H_5, C_2H_5O, p Cl-C_6H_4

R = C_2H_5, C_4H_9

These ketenimines are quite reactive, and readily undergo hydrolysis and alcoholysis. With reactive halides, the alkyl metal halide and substituted malononitriles are obtained.

$$R^1CH_2C(CN){=}C{=}N\text{-}MR_3 \xrightarrow{R''OH} R^1CH_2C(CN)_2H + R''OMR_3 \qquad (7)$$

$$R^1CH_2C(CN){=}C{=}N\text{-}MR_3 \xrightarrow{R'''Cl} R^1CH_2C(CN)_2R''' + ClMR_3 \qquad (8)$$

R'' = H, C_2H_5

R''' = $CH_3CH{=}CHCH_2Cl$, C_6H_5COCl, $C_6H_5CH_2Cl$

Abel, et. al.,[36] have reported 1,4-addition of certain organometallic bases and other compounds such as $(Me_2N)_3B$, Me_3SiSMe to $(CF_3)_2C{=}C(CN)_2$ and $(CF_3)(CF_2Cl)C{=}C(CN)_2$ to produce ketenimines under mild conditions.

Reactions (7) and (8) above are analogous to certain ones involved in this research and will be referred to again later.

The activated olefin, acrylonitrile, which has been used in this work, is known to form complexes with transition metals. Schrauzer[37] reported the formation of a bisacrylonitrile nickel complex, a pyrophoric substance obtained from refluxing $Ni(CO)_4$ and acrylonitrile. The absence of the intense vinyl absorption in the 900-1000 cm^{-1} region indicated that the π-electrons of the double bond in acrylonitrile were involved in the bonding. The nitrile absorption was found at 2220 cm^{-1}, shifted slightly from 2245 cm^{-1} in liquid acrylonitrile. Yamamoto[38] obtained a 1:1 adduct using diethyldipyridylnickel and acrylonitrile. This orange adduct, which dissociates at -78°, was reported to be an active catalyst for the polymerization of acrylonitrile. Dewhirst[39] studied the reaction of acrylonitrile with ethanolic $RhCl_3$ and obtained a chloro-bridged product of approximate composition $(CH_2{=}CH\text{-}CN)_2RhCl_2$, wherein one of the acrylonitrile moieties was believed to be σ-bonded to Rh(III) and the other perhaps π-bonded since it could be displaced by pyridine to yield $(CH_3CHCN)RhCl_2(C_5H_5N)_3$. This reaction was thought to involve an intermediate Rh(III) hydride, and to provide evidence for his above formulation he allowed $(MePh_2As)_3RhHCl_2$ to react with acrylonitrile. The product obtained, $(MePh_2As)_3Rh(CH_3CHCN)Cl_2$, reacted with pyridine to give $(CH_3CHCN)RhCl_2(C_5H_5N)_3$.

The two latter citations are of interest because intermediates in the polymerization of olefins by Ziegler-Natta catalysts and other transition metal catalysts have been postulated to contain a σ-bonded

and a π-bonded organic moiety.[40] The results reported herein show that such a model intermediate which is relatively stable can be formed by the reaction of acrylonitrile with the hydrido-iridium substrates.

The latter portion of the work for this Dissertation covers the research begun on the reactions of acetylenes with $IrH(CO)(Ph_3P)_3$ and $IrH(CO)_2(Ph_3P)_2$. Although the investigation has not been extensive, there are indications that an interesting variety of types of compounds can be produced depending on the iridium complex used, the nature of the acetylene and the reaction conditions.

A cursory survey of the literature reveals that many of the transition metal hydrides, and especially the carbonyl hydrides of Mn, Co, and Re, react readily with acetylenes via insertion reactions to give σ-vinyl derivatives.[41]

The only known reaction of acetylenes* with hydridoiridium complexes concerned the hydrogenation of acetylene to ethylene and ethane with $IrH(CO)(Ph_3P)_3$ as catalyst.[42] However, as a catalyst it was found to be inefficient because of a concurrent and irreversible reaction with the acetylene, and no intermediate complex was isolated.

In the work described herein it was found that $PhC{\equiv}CH$ reacts with the iridium substrates to form a hydrido-diacetylido-complex. This is of particular interest since Meriwether, et. al.,[43] have proposed such a type of compound as an intermediate in the linear polymerization of

---

* At the time of writing, a preliminary communication reporting reactions of alk-1-ynes with hydridoiridium complexes was published.[71] This work will be referred to in the Results and Discussion section.

monosubstituted acetylenes. They postulated that a hydrido-nickel complex containing a σ-bonded acetylide group was the "active" catalyst formed from the nickel-carbonyl-phosphine complex used in the polymerization reactions.

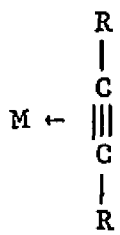
Generally, σ-bonded acetylene complexes are prepared by metathetical reactions between the metal halide and an alkali metal acetylide in liquid ammonia and acetylides of Cr, Mo, W, Pt, and Pd, have been prepared in this way.[44] The formation of an acetylide from $IrCl(CO)(Ph_3P)_2$ by an addition reaction has been reported.[45] When $HC{\equiv}CCO_2Et$ and the iridium complex are heated in benzene at 50° for 15 hr, a hydrido-monoacetylide complex is obtained. The σ-bonded acetylide moiety in this compound exhibits a characteristic strong band at 2130 cm^{-1}.

The same authors reacted $PhC{\equiv}CH$ with $IrCl(CO)(Ph_3P)_2$ for 15 hr at 80°, but the isolation of an intermediate iridium-acetylene species was not attempted. The iridium was recovered as $IrCl_3(CO)(Ph_3P)_2$ by the action of HCl on the reaction mixture, and the remaining solution yielded polyphenylacetylene which was identified by elemental analysis and by its infrared spectrum which was similar to that reported by Okamoto[46] for polyphenylacetylene obtained by thermal polymerization of the neat acetylene.

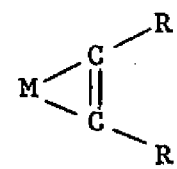
Furlani, et. al.,[47] found that cis- and trans-$PtCl_2(Ph_3P)_2$, trans-$PtHCl(Ph_3P)_2$, $Pt(Ph_3P)_4$, and $Pt(CH{\equiv}CPh)(Ph_3P)_2$ acted as catalysts for the polymerization of bulk phenylacetylene at reflux temperatures, the reaction being completed within 5 hr. At room temperature, these compounds reacted with $PhC{\equiv}CH$ without polymerization to produce mainly

trans-$Pt(C{\equiv}CPh)_2(Ph_3P)_2$, and small amounts of the cis-isomer. The chloro compounds also produced some $PtCl(C{\equiv}CPh)(Ph_3P)_2$. These acetylide complexes were assumed to be the "active" catalysts, and a polymerization scheme was advanced which did not involve a hydride complex as did Meriwether's scheme previously mentioned. Instead, a molecule of the monomer unit would π-bond as a fifth ligand to the active catalyst and subsequently insert into the Pt-acetylide bond to effect dimerization and eventually polymerization as this process continued.

Acetylenes can also react by forming π-bonds with transition metals, and many of these types of complexes have been reported in the literature over the past 20 years. As with π-bonded olefins, two extreme bond types have been postulated for coordinated acetylenes. In structure III, the acetylene is thought to act as a monodentate ligand[48] whereas in IV, the acetylene is assumed to be doubly σ-bonded with



III



IV

resulting angular distortion.[49] These structures have been suggested on the basis of infrared stretching frequencies wherein acetylenes bonded as in III exhibit a lowering of 130-200 cm^{-1} from the range 2260-2190 cm^{-1} normally exhibited[50] by disubstituted acetylenes. If the acetylene is strongly coordinated as in IV, the triple bond

stretching frequency is lowered by ca. 500 cm^{-1}, and such frequencies around 1700 cm^{-1} have been compared to small ring endocyclic olefins.[27] According to Collman,[45] the question is unsettled as to whether the two bond types, III and IV, represent energy minima and could be found in valence tautomerism or whether these are extreme discriptions of a gradual transformation. Since reported infrared stretching frequencies among coordinated acetylenes are scattered over the range 2060 to 1600 cm^{-1}, Collman proposes a gradual change rather than two distinct bond types.

Before proceeding with the report of the work involved in this Dissertation, a brief discussion of two of the iridium substrates used herein would be in order.

The hydrido-complex, $IrH(CO)(Ph_3P)_3$, first formed by reduction of $IrCl(CO)(Ph_3P)_2$ with 95% aqueous hydrazine,[51] is isostructural with $RhH(CO)(Ph_3P)_3$, whose x-ray crystal structure[52] shows it to be trigonal bipyramidal with H anc CO in the trans position. The resonance of the hydridic proton in the iridium complex shows a 1:3:3:1 quartet structure (δ = -11.2 ppm, J_{P-H} = 42 Hz); accordingly, a trigonal bipyramidal structure is implied.

This iridium complex is a catalyst for the hydrogenation of alk-1-enes,[42] but it is not as effective as the corresponding rhodium analogue. In the scheme proposed by O'Connor and Wilkinson[53] for hydrogenations using $RhH(CO)(Ph_3P)_3$, prior dissociation of a Ph_3P to produce a coordinatively unsaturated species is necessary for alkene coordination, and this dissociation is not readily undergone by the iridium analogue at moderate temperatures.

The crystal structure analysis[54] of the orthorhombic form of $IrH(CO)_2(Ph_3P)_2$ shows a distorted trigonal bipyramid in which a P atom and the hydride hydrogen occupy the axial positions. In solution, the infrared spectra suggest different forms or isomeric species of $IrH(CO)_2(Ph_3P)_2$, and on the basis of nmr studies in different solvents and at different temperatures, Yagupsky and Wilkinson[55] concluded that this complex exhibits isomeric fluxional behavior, existing in forms with C_s and C_{2v} symmetry. The high field nmr signal observed for this compound depends on the solvent used and the mole fraction of the isomeric forms present in solution. The observed triplet is an average of two separate triplets and only J_{AV} values were given.

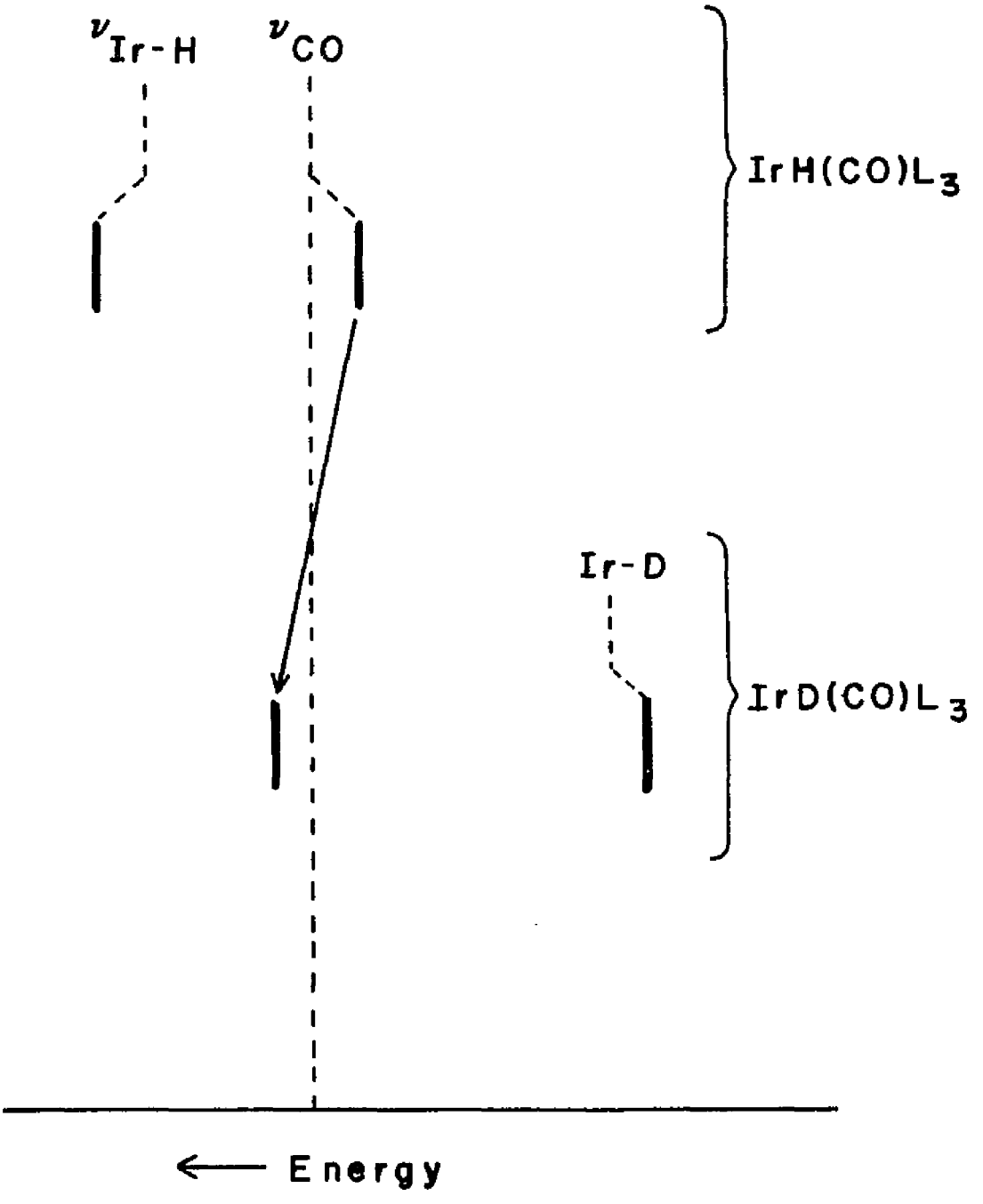
For the work reported herein, combined nmr and infrared studies have aided in the elucidation of the stereochemistry for some of the compounds, or else have allowed a certain amount of speculation regarding them. The presence of a carbonyl group in the hydrido-complexes is a useful probe and has been used effectively by Vaska[56,57] in arriving at probable structures of complexes. If the carbonyl stretching frequency is shifted in going from the hydrido- to the corresponding deuterido-complex, a <u>trans</u> H-CO arrangement is signified. Braterman and coworkers[58] utilized this same effect in their assignments of infrared bands for $HRe(CO)_5$. An explanation analogous to theirs but applied to the hydridoiridium complexes where $\nu_{Ir-H} > \nu_{CO}$, can be followed by reference to Figure I.

In $IrH(CO)(Ph_3P)_3$ the ν_{Ir-H} and ν_{CO} stretching modes, if belonging to the same symmetry species (vertical dotted

lines, top row of figure) will mix and produced observed bands at higher and lower energies (vertical solid lines, second row of Figure 1). In $IrD(CO)(Ph_3P)_3$, however, the purely carbonyl symmetry coordinate is separated by a large amount from the Ir-D symmetry coordinate. Their mixing will be much decreased, and the observed bands (solid vertical lines, last row of figure) will suffer smaller energy shifts from the positions of the unmixed coordinates. Therefore, the carbonyl band is observed to shift to higher energy (diagonal arrow) when ν_{Ir-H} is replaced by ν_{Ir-D} in going from $IrH(CO)L_3$ to $IrD(CO)L_3$.

Figure 1

Representation of observed shift (diagonal arrow) for ν_{CO} in going from $IrH(CO)L_3$ to $IrD(CO)L_3$.


ν_{Ir-H}
ν_{CO}
IrH(CO)L$_3$
Ir-D
IrD(CO)L$_3$
← Energy

EXPERIMENTAL - GENERAL

This section includes information on general procedures, techniques, and references to the preparation of known starting materials. Where modifications of the literature methods are introduced, a description is given. The preparation of new compounds is described in the next section.

General Procedures

Most reactions and recrystallizations were carried out under a nitrogen atmosphere using the types of glassware and techniques described elsewhere.[59] The filtrations were usually done in the open atmosphere, unless stated otherwise.

Reaction times and conditions for many of the syntheses were established by infrared monitoring of samples withdrawn from the reaction vessel.

Deuterido-complexes were utilized for diagnostic purposes only to indicate the presence or absence of Ir-H bonds, and these compounds were not fully characterized in themselves.

Silica gel (0.05-0.20 mm) 70-325 mesh ASTM was utilized for column chromatography. Thin layer chromatography using SilicAR TLC-4GF on microscope slides was utilized to establish solvent systems for column chromatography and to indicate the relative purity of samples. In general, chromatography was not used with the cyanoolefin complexes. Although impurities could be separated, no convenient solvent system

was found to be satisfactory to move the desired compound on a column or on a thin layer slide.

Instrumentation

Infrared spectra were obtained using a Beckman IR-7 instrument. Spectra of solutions of the compounds were obtained using ca. 0.2 mm NaCl solution cells and measuring versus neat solvent. Solids were also analyzed as either Nujol or hexachlorobutadiene (HCBD) mulls. The following abbreviations used to describe spectral band intensities and band widths are: vs - very strong; s - strong; m - medium; w - weak; sp - sharp; br - broad; and sh - shoulder. All band positions are given in cm^{-1}.

Proton nuclear magnetic resonance spectra were obtained with Varian Models A-60A and HA-100 spectrometers. Saturated solutions of the complexes in $CDCl_3$ (for low field spectra) or in CH_2Cl_2 (for high field spectra) were used with tetramethylsilane as an internal standard.

Melting points were taken on a Fisher-Johns apparatus and are uncorrected.

Molecular weights were determined with a Hewlett-Packard Mechrolab Model 302 Osmometer in chloroform using a 37° Non-Aqueous probe. Because of the limited solubility of most of the compounds studied, a calibration plot was constructed for the range to 0.012 molal using triply recrystallized benzil.

Elemental Analysis

Carbon, hydrogen, and nitrogen analyses were done by Mr. Ralph Seab of Louisiana State University. Analyses for phosphorus, nitrogen and fluorine were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Materials

The iridium salts were purchased from Alfa Inorganics, Inc., Beverly, Massachusetts and from Engelhard Industries, Newark, New Jersey.

Tetracyanoethylene (TCNE) was recrystallized from boiling chlorobenzene and sublimed before use. Phenylacetylene was distilled from KOH. Benzene was stored over sodium. All other solvents and chemicals used were of reagent grade quality.

Trans-chlorocarbonylbis(triphenylphosphine)iridium(I), $IrCl(CO)(Ph_3P)_2$, was prepared by Method B of Collman and Kang.[45]

Hydridocarbonyltris(triphenylphosphine)iridium(I), $IrH(CO)(Ph_3P)_3$, was prepared in over 90% yield using $NaBH_4$ as the hydride source and is an improvement on the original preparation[51] using hydrazine.

To a suspension of trans-$IrCl(CO)(Ph_3P)_2$ (1.5 g, 1.92 mmoles) containing Ph_3P (1.96 g, 7.5 mmoles) in ethanol (40 ml) at 60-65° was added $NaBH_4$ (ca. 1.5 g) in portions with stirring over a 20 min interval. After another hour of stirring, or until a test portion of the suspended yellow solid showed no band in the ir at 1955 cm^{-1} [due to trans-$IrCl(CO)(Ph_3P)_2$], the warm reaction mixture was filtered,

washed with two portions (20 ml) each of ethanol, warm water, ethanol, and dried to a bright yellow solid, mp 185°. The ir (HCBD mull) pattern included bands at 2090 w (ν_{Ir-H}) and 1930 vs (ν_{CO}) cm^{-1}.

Recrystallization from benzene-ethanol resulted in a dull yellow compound of mp 162° (air-dried) with bands at 2125 w (ν_{Ir-H}) and 1920 vs (ν_{CO}) cm^{-1}. After drying at 80° in vacuo, the compound reverted to bright yellow having the same ir pattern, but mp of 185°. A benzene solution spectrum exhibited bands at 2070, and 1930 cm^{-1}.

Malatesta[60] reported the following data for two different forms of this compound. The first two spectra were taken as mulls, the third in benzene solution.

ν_{Ir-H}	ν_{CO}	mp °C	Recrystallized from:
2120	1920	145	chloroform-hexane
2090	1935	161	benzene-ethanol
2070	1930	(benzene solution)	

Although there is disagreement with the literature values for the spectra and mp of the solids, the solution spectra were in agreement.

Trihydridocarbonylbis(triphenylphosphine)iridium(III), $IrH_3(CO)(Ph_3P)_2$.

It is known that $IrCl(CO)(Ph_3P)_2$ disproportionates considerably during reduction with hydrazine[51] to yield the yellow compound, $IrH(CO)(Ph_3)_3$. The following modified literature method[60] eliminates this possibility to a great extent and results in the formation of a white compound.

Sodium borohydride (1.5 g) was suspended in reagent grade tetrahydrofuran (35 ml) at room temperature, and trans-$IrCl(CO)(Ph_3)_2$ (1.5 g, 1.92 mmoles) was added in small portions at a rate such that the solution became colorless before further addition. Stirring was continued for an hour after the final addition. After filtering under N_2, and washing the residue with two portions (20 ml) of THF, the combined filtrates were evaporated to dryness under reduced pressure and the flask then filled with N_2. The residue was dissolved in 8 ml dry benzene, and with the addition of 70-80 ml of hexane followed by cooling, 1.39 g of the white compound was collected.

In comparing the ir pattern to that given in the literature, the above compound appears to be a mixture of isomers. However, since the low melting point form was reported to be unstable in benzene, the compound was used without further recrystallization.

	ν_{Ir-H}	ν_{CO}	δ_{Ir-H}	mp °C
Found:	2115,2073,1775-80	1954	860-53-46-21-809(Nujol)	148
Literature:[60]	2118,2080	1960	850-840-820-800	132
	2080,1785*	1965	845-802	145
	2080,1780*	1955	(benzene solution)	

* The broad band at 1780-85 was attributed to a polyhydric species with two hydrogens in the trans position.

Hydridodicarbonylbis(triphenylphosphine)iridium(I), $IrH(CO)_2(Ph_3P)_2$.

Attempts were made to synthesize the yet unknown, but erroneously reported, $IrH(CO)(Ph_3P)_2$ according to literature methods.[60]

Of the five different methods cited, one involving the carbonylation of iridium(IV) iodide followed by reflux with Ph_3P in ethanolic KOH, could not be duplicated, a failure shared and reported by Harrod, et. al.[61] Another method, involving bubbling N_2 through a cold benzene solution of $IrH_3(CO)(Ph_3P)_2$ for 4 hr, was tried, but 8 hr treatment with N_2 only served to transform the mixture of isomers in the starting material to the pure high melting point form.

It was found, however, that CO bubbled through a benzene solution of $IrH_3(CO)(Ph_3P)_2$ served to remove H_2, a reaction analogous to another reported method of converting $IrH_3(Ph_3P)_2$ to $IrH(CO)(Ph_3P)_2$ by means of CO. Since the former trihydride could be prepared in better yield, it was used for in situ preparations of the desired product, but in its reactions there were indications that it was not a monocarbonyl species.

Before resumption of further investigation on this compound, Yagupsky and Wilkinson[55] reported essentially the same, but a more direct way of preparing the compound, i.e., carbonylation of $IrH_3(CO)(Ph_3P)_2$ prepared in situ from $IrCl(CO)(Ph_3P)_2$ and $NaBH_4$. The study by them showed the compound was actually $IrH(CO)_2(Ph_3P)_2$, and their method was used for subsequent preparations.

Deuteridocarbonyltris(triphenylphosphine)iridium(I), $IrD(CO)(Ph_3P)_3$.

This was usually prepared in small amounts (< 0.5 g) as needed by a method similar to that given above for $IrH(CO)(Ph_3P)_3$

but with some modifications. A 1:2 weight ratio of $NaBD_4$:$IrCl(CO)(Ph_3P)_2$ was used, but final stirring was continued for 3-4 hr. No appreciable H-D exchange was incurred by using ethanol as solvent. The reaction mixture was evaporated to dryness under reduced pressure, extracted with benzene, filtered and concentrated to a small volume. The addition of ethanol precipitated the product which was used without further recrystallization. The ν_{CO} was found (Nujol) at 1936 cm^{-1}; the literature value[60] is 1943 cm^{-1}.

Deuteridodicarbonylbis(triphenylphosphine)iridium(I), $IrD(CO)_2(Ph_3P)_2$ was prepared by the action of CO on $IrD(CO)(Ph_3P)_3$, by an adaptation of Method A of Yagupsky and Wilkinson[55] for the preparation of $IrH(CO)_2(Ph_3P)_2$ from $IrH(CO)(Ph_3P)_3$. The literature values for ν_{CO} are: 1925, 1945, 1975, and 2008 (in C_6H_6). Found: 1925, 1934-45, 1975, and 2012 (in CH_2Cl_2).

Chlorocarbonylbis(triphenylarsine)iridium(I), $IrCl(CO)(Ph_3As)_2$, was prepared according to a literature method.[55]

Trihydridocarbonylbis(triphenylarsine)iridium(III), $IrH_3(CO)(Ph_3As)_2$.

The literature method[62] for the production of this compound from $IrBr(CO)(Ph_3As)_2$ and $NaBH_4$ yielded a dark brown compound when this method was applied to $IrCl(CO)(Ph_3As)_2$. The method was modified as follows.

Sodium borohydride (0.1 g, 2.7 mmoles) was added to a suspension of $IrCl(CO)(Ph_3As)_2$ (0.42 g, 0.5 mmole) in 20 ml of warm

(60°) ethanol. After a few minutes of stirring, benzene was added to just dissolve the yellow complex and this resulted in an immediate discharge of color. The solution was evaporated to ca. 1/3 volume whereupon precipitation of the compound followed. It was collected and washed with several portions each of ethanol, water, ethanol and air dried to give an 86% yield of the white product. The Nujol mull spectrum included bands at 2135 m, 2090 m, 2050 s (ν_{Ir-H}) and 1945 vs (ν_{CO}) cm^{-1}, in agreement with the literature values.[62] The benzene solution spectrum included bands at 2073 vs, 2090 s, sh, 2105 s, sh (ν_{Ir-H}) and 1973 m (ν_{CO}) cm^{-1}.

EXPERIMENTAL: PREPARATION AND CHARACTERIZATION OF COMPLEXES

Complexes Derived from Olefins

Hydridocarbonyl(fumaronitrile)bis(triphenylphosphine)iridium, $IrH(CO)(NCCH{=}CHCN)(Ph_3P)_2$.

Fumaronitrile (0.39 g, 5.0 mmoles) and $IrH(CO)(Ph_3P)_3$ (0.5 g, 0.5 mmole) were stirred together in 10 ml of benzene at 40-50°. The bright yellow solution turned colorless and within a few minutes some white solid began to form. After another half-hour of stirring, 30 ml of ethanol was added and the solid was collected and washed with ethanol. Yield, 0.4 g (97%). It was recrystallized from CH_2Cl_2-CH_3OH to give colorless needles, mp 232° (dec). Anal. Calcd for $C_{41}H_{33}IrN_2OP_2$: C, 59.77; H, 4.04; N, 3.40; P, 7.52; mol wt, 824. Found: C, 59.39; H, 4.23; N, 3.31; P, 7.53; mol wt, 849.

The same compound was obtained by treating a benzene solution of $IrH(CO)_2(PH_3P)_2$ with a five-fold excess of fumaronitrile. Carbon monoxide gas was evolved at room temperature and warming the solution was not required.

The complex, $IrH_3(CO)(Ph_3P)_2$, reacted more slowly with fumaronitrile with the evolution of tiny bubbles of hydrogen beginning at 40-50°. At this temperature the white compound appeared after a half-hour, but apparently the reaction was not complete within an hour, as evidenced by the low yield (53%).

Deuteridocarbonyl(fumaronitrile)bis(triphenylphosphine)iridium was prepared from IrD(CO)(Ph_3P)$_3$ as previously mentioned.

Hydridocarbonyl(fumaronitrile)bis(triphenylarsine)iridium, IrH(CO)(NCCH=CHCN)(Ph_3As)$_2$.

Fumaronitrile (0.24 g, 3.0 mmoles) and $IrH_3(CO)(Ph_3As)_2$ (0.5 g, 0.6 mmole) were heated to 80-90° in 30 ml of benzene for nearly 2 hr. The mixture was carefully monitored and at the appearance of a band in the ir at 2037 cm^{-1}, the reaction was stopped. The solution was evaporated to dryness under reduced pressure and the residue was washed with ethanol. The residue was recrystallized from CH_2Cl_2-MeOH to give 0.4 g (73%) of an off-white product, mp 190-195° (dec). Anal. Calcd for $C_{41}H_{33}As_2IrN_2O$: C, 54.08; H, 3.65; N, 3.07. Found: C, 53.48; H, 3.54; N, 3.00.

The temperature and time of reaction were crucial for the preparation of this complex. There was almost quantitative recovery of the unchanged trihydride complex after the starting materials were warmed together in benzene at 50-60° for an hour. When the reactants were heated for 2 hr at 110-120° in toluene, a product, not as yet characterized, was obtained whose ir spectrum exhibited a strong band at 2037 and a medium band at 2216 cm^{-1}, but no band ascribable to ν_{Ir-H}. The nmr spectrum showed no high field signal, but two unsplit doublets centered at 3.6 and 3.8 ppm (J = 8 Hz) were observed in addition to the phenyl proton signals and these doublets were assigned

to a π-bonded fumaronitrile group. As it turned out, the solution spectrum, but not the mull spectrum of the hydrido-fumaronitrile complex and of the starting material, $IrH_3(CO)(Ph_3As)_2$, have ν_{IR-H} and ν_{CO} values very nearly the same and it was difficult to judge from the ir spectrum of a monitored sample whether the starting material had completely reacted. The above procedure was developed whereby the reaction was stopped at the appearance of the band at 2037 cm^{-1}.

Hydridocarbonyl(cinnamonitrile)bis(triphenylphosphine)iridium, $IrH(CO)(C_6H_5CH=CHCN)(Ph_3P)_2$.

Cinnamonitrile (2.5 ml, 19 mmoles), $IrH(CO)(Ph_3P)_3$ (0.25 g, 0.25 mmole) and benzene (2.5 ml) were warmed together at 50° for 1 hr. The volume of the solution was then reduced until an oily residue resulted, and this was taken up in benzene-hexane to give 0.18 g (75%) of a beige solid. Recrystallization from benzene-hexane produced an off-white complex, mp 145°. Anal. Calcd for $C_{46}H_{38}IrNOP_2$: C, 63.13; H, 4.38; N, 1.60; P, 7.08. Found: C, 63.81; H, 4.77; N, 1.65; P, 6.82.

The compound was also obtained from $IrH(CO)_2(Ph_3P)_2$, and deuteridocarbonyl(cinnamonitrile)bis(triphenylphosphine)iridium was obtained from $IrD(CO)(Ph_3P)_3$.

Reaction of $IrH(CO)(C_6H_5CH{=}CHCN)(Ph_3P)_2$ with fumaronitrile.

When an ethanolic suspension of this complex was heated for a few minutes at 50° in the presence of fumaronitrile, a more granular suspension resulted. The recovered product was shown by its mp and infrared spectrum to be $IrH(CO)(NCCH{-}CHCN)(Ph_3P)_2$.

Hydridocarbonyl(benzylidenemalononitrile)bis(triphenylphosphine)iridium, $IrH(CO)[C_6H_5CH{=}C(CN)_2](Ph_3P)_2$.

When $C_6H_5CH{=}C(CN)_2$ (0.77 g, 5 mmoles) was added to $IrH(CO)(Ph_3P)_3$ (0.5 g, 5.0 mmoles) in 10 ml of benzene, a very dark yellow solution resulted after heating at 60-70° for 1 hr. The addition of 35 ml of MeOH to the cooled solution resulted in the precipitation of a pale yellow solid which was filtered and washed with MeOH. Yield, 0.36 g (80%).

Recrystallization from CH_2Cl_2-MeOH produced a white microcrystalline product admixed with a small amount of pale yellow crystals. Anal. Calcd for $C_{47}H_{37}IrN_2OP_2$: C, 62.70; H, 4.15; N, 3.11; mol wt, 900. Found: C, 62.13; H, 3.98; N, 2.94; mol wt, 933.

The Nujol infrared spectra of the uncrystallized material showed split bands for ν_{CO}, $\nu_{Ir\text{-}H}$, and ν_{CN} in the region 1900-2250 cm^{-1}, whereas for the recrystallized material, one set of bands was reduced to shoulders. In further preparations of this compound under different

conditions, it became apparent that different forms or isomers were being produced, the more soluble pale yellow crystals having a higher melting point (165-185°) and a different solid state infrared spectrum, but an identical CH_2Cl_2 solution spectra, and the same analysis as for the less soluble white low melting point form (135-145°).

If a fraction containing mostly the high melting point form was recrystallized, both forms could be obtained, and no one pure form was isolated. In one preparation carried out at room temperature, a relatively pure white form (mp 138-140°) precipitated from a benzene solution. It reverted in the solid state in a weeks' time to what appeared to be a mixture of forms by its infrared and nmr spectrum.

The complex, $IrH(CO)_2(Ph_3P)_2$, did not give the same compound with $C_6H_5CH=C(CN)_2$. This reaction will be described later. The complex $\underline{IrD(CO)[C_6H_5CH=C(CN)_2](Ph_3P)_2}$ was prepared from $IrD(CO)(Ph_3P)_3$ as above. The infrared spectrum showed the presence of more than one form.

<u>Reaction of $IrH(CO)[C_6H_5CH=C(CN)_2](Ph_3P)_2$ with Fumaronitrile</u>.

Fumaronitrile was added to a CH_2Cl_2 solution of this complex at room temperature and readily replaced $C_6H_5CH=C(CN)_2$. After evaporating the CH_2Cl_2 to a small volume and adding MeOH, a white product formed which was shown to be $IrH(CO)(NCCH=CHCN)(Ph_3P)_2$ by its mp and infrared spectrum.

Chlorocarbonyl(fumaronitrile)bis(triphenylarsine)iridium, $IrCl(CO)(NCCH{=}CHCN)(Ph_3As)_2$.

Fumaronitrile (0.39 g, 5.0 mmoles) and $IrCl(CO)(Ph_3As)_2$ (0.21 g, 0.25 mmole) were stirred together in 5 ml of CH_2Cl_2. When the yellow solution became colorless, it was evaporated to dryness and the residue washed with EtOH. Yield, 0.22 g (81%). It was recrystallized from CH_2Cl_2-EtOH to yield a white product, mp, 255-260° (dec). Anal. Calcd for $C_{41}H_{31}As_2IrN_2O$: C, 52.01; H, 3.41; N, 2.96. Found: C, 52.00; H, 3.31; N, 2.81.

The Nujol mull spectrum of this complex included bands at 2011 vs (ν_{CO}) and 2210 m, 2225 sh (ν_{CN}) cm^{-1}.

Reaction of $IrCl(CO)(Ph_3As)_2$ with Acrylonitrile.

One ml of acrylonitrile containing $IrCl(CO)(Ph_3As)_2$ (0.1 g, 0.12 mmole) was stirred for a few minutes at room temperature. The bright yellow solution became almost colorless and a beige solid began to form. After 10 min, 5 ml of hexane was added. The solid was collected and washed with hexane to yield 0.1 g (90%) of an off-white product, mp, 200° (dec). Anal. Calcd for $C_{40}H_{33}As_2ClIrNO$: C, 52.16; H, 3.61; N, 1.52. Found: C, 50.90; H, 3.42; N, 1.18.

Bands were observed in the Nujol mull spectrum at 2208 m (ν_{CN}) and 2020 vs (ν_{CO}) cm^{-1}. A benzene solution of this complex is bright yellow indicating dissociation. In addition to bands at 2212 m (ν_{CN}) and 2011 s (ν_{CO}), a very strong band at 1960 cm^{-1} (due to $IrCl(CO)(Ph_3As)_2$) was observed in the solution spectrum.

Reaction of $IrCl(CO)(Ph_3As)_2$ with Benzylidenemalononitrile.

Three milliliters of benzene containing the iridium complex (0.1 g, 0.12 mmole) and $C_6H_5CH=C(CN)_2$ (0.15 g, 1.0 mmole) was warmed to 50° for 1 hr. The colorless solution was evaporated to dryness under N_2 and the excess olefin was removed by washing with ethanol leaving 0.1 g (80%) of a light yellow residue, mp, 255°. Anal. Calcd for $C_{47}H_{36}As_2ClIrN_2O$: C, 55.22; H, 3.55; N, 2.74. Found: C, 58.73; H, 3.82; N, 2.36.

The complex dissociates considerably in benzene solution as evidenced by the very strong band at 1960 cm^{-1} and only weak bands at 2212 (ν_{CN}) and 2005 (ν_{CO}) cm^{-1}.

Reaction of $IrCl(CO)(Ph_3As)_2$ with Cinnamonitrile.

The iridium complex was recovered unchanged when hexane was added to a benzene solution of these reactants which had been warmed to 50-60° for 2 hr. However, the infrared spectrum of a withdrawn sample of the reaction mixture indicated some degree of complexation had taken place. In addition to the strong band at 1960 cm^{-1} due to the starting material, an equally strong band at 2008 cm^{-1} was observed and this was attributed to ν_{CO} in the complex.

Formation of $[IrH_2(CO)(Ph_3P)_3]^+$ and $[IrH_2(CO)_2(Ph_3P)_2]^+$ Using Maleic and Cinnamic Acids.

The addition of maleic and cinnamic acids to dichloromethane solutions of $IrH(CO)(Ph_3P)_3$ or $IrH(CO)_2(Ph_3P)_2$ resulted in the formation of known cationic hydrido-complexes. These were not isolated but were detected in solution by infrared and nmr. The infrared spectral bands observed for the cationic species are compared to the literature values below:

	ν_{Ir-H}	ν_{CO}	Medium
$[IrH_2(CO)(Ph_3P)_3]^+$			
Observed:	2160sh,2114s	2012s	CH_2Cl_2
Literature:[60]	2155,2118	2011	mull
$[IrH_2(CO)_2(Ph_3P)_2]^+$			
Observed:	sh2170m,2155s	2085s,2055s	CH_2Cl_2
Literature:[63]	2180s,sh2155m	2085s,2050s	KBr

When trichloroacetic acid was added to CH_2Cl_2 solutions of these iridium substrates, the identical corresponding infrared patterns were observed and these data are additional evidence that the main species formed in the maleic and cinnamic acid reactions are the cations rather than the π-bonded olefin complexes.

Additional infrared bands were detected in the solutions containing cinnamic acid. A summary of the above reactions and results is given in the Results and Discussion section.

Hydridocarbonyl(fumaric acid)bis(triphenylphosphine)iridium, $IrH(CO)(HOOCCH{=}CHCOOH)(Ph_3P)_2$.

A warm (70°) solution of $IrH(CO)(Ph_3P)_3$ (0.25 g, 0.25 mmole) in 2 ml of benzene was added drop-wise with stirring to 1.5 ml of an ethanol solution of fumaric acid (0.058 g, 0.5 mmole). A clear colorless solution was obtained initially, but it changed to pale yellow and a white precipitate formed as the addition was completed. The mixture was cooled to room temperature, filtered and the residue washed with ethanol. Yield, 0.11 g, (50%), mp 192-195° (dec). Anal. Calcd for $C_{41}H_{35}IrO_5P_2$: C, 57.12; H, 4.10. Found: C, 56.70; H, 4.11.

An infrared spectrum of the filtrate showed bands corresponding to the cation $[IrH_2(CO)(Ph_3P)_3]^+$.

The complex $IrH(CO)(HO_2CC{=}CCO_2H)(Ph_3P)_2$ is sparingly soluble in benzene, dichloromethane and methanol and no nmr spectrum could be obtained.

The complex, $IrH(CO)_2(Ph_3P)_2$, was allowed to react in a similar fashion with fumaric acid and yielded the same product.

Reaction of $IrH(CO)(HO_2CC{=}CCO_2H)(Ph_3P)_2$ with Fumaronitrile.

A sample of the complex was suspended in ethanol containing excess fumaronitrile and heated to 70°. A clear solution resulted which, upon cooling, deposited crystals of $IrH(CO)(NCCH{=}CHCN)(Ph_3P)_2$.

(Cyano[dicyanomethyl]keteniminato)carbonyl(tetracyanoethylene)bis-(triphenylphosphine)iridium, $Ir(C_6N_4H)(CO)[C(CN)_2{=}C(CN)_2](Ph_3P)_2$.

(The following method was developed after many attempts were made to establish the optimum conditions for the preparation of this compound. Because of several faulty nitrogen analyses from a commercial firm, it was assumed that this compound was a 1:1 adduct and consequently insufficient TCNE was used in many of the trials. This, along with using ethanol as an aid to precipitation, produced impure material which could not be adequately purified to give consistent analyses. Apparently, ethanol altered the course of the reaction somewhat, and one of the side-products produced was isolated. In a study of the effect of alcohol on the reaction, it was found that if alcohol were added shortly after the addition of TCNE to the benzene solution of the iridium complex, rather high yields of this side-product could be obtained. One of these experiments will be described, because an attempt was made to characterize the product.) The following is the method for producing the keteniminato-complex.

a. Drop-wise addition of a benzene solution of $IrH(CO)_2(Ph_3P)_2$ to a four-fold excess of TCNE in benzene at room temperature produced a deep orange solution as bubbles of CO gas were evolved and simultaneously an orange-yellow solid separated. After 0.5 hr of stirring, the solid was collected, washed with ethanol and recrystallized from

CH_2Cl_2-C_6H_6 to give bronze-colored crystals. Yield, 70%; mp 165-180° (dec). Anal. Calcd for $C_{49}H_{31}IrN_8OP_2 \cdot \frac{1}{2}C_6H_6$*: C, 59.99; H, 3.29; N, 10.76; P, 5.95; mol wt, 1040. Found: C, 58.68; H, 2.97; N, 10.68; P, 5.86; mol wt, 904.

b. The above method with $IrH(CO)(Ph_3P)_3$ resulted in the formation of a dark gum, but a 10% yield of the desired product was obtained by adding hexane to the remaining benzene solution. A higher yield was obtained in those reactions wherein solid TCNE was added to the benzene solution of the iridium complex, but ethanol was used in these reactions and the product was impure.

c. Solid TCNE added to a benzene solution of $IrD(CO)(Ph_3P)_3$ produced a compound having the same infrared pattern in the 1900-2250 cm^{-1} region as the keteniminato-complex.

d. With $IrH_3(CO)(Ph_3P)_2$, a small yield (< 10%) of the complex precipitated from the benzene solution after the reactants were warmed for 0.5 hr at 45-50°. When ethanol was added to the filtrate, which then stood for several hours, a pale yellow precipitate formed. This material was extracted with CH_2Cl_2 (in which it was almost insoluble) leaving a white residue which showed ν_{CN} and ν_{CO} but no $\nu_{N=C=C}$ bands in the 1900-2250 cm^{-1} region.

---

* The X-ray study[64] shows that the crystals contain one molecule of benzene per two iridium atoms.

Cyanocarbonyl(tetracyanoethylene)bis(triphenylphosphine)iridium, $Ir(CN)(CO)[C(CN)_2{=}C(CN)_2](Ph_3P)_2$. (Formulation tentatively assigned.)

(a) The complex $IrH(CO)_2(Ph_3P)_2$ (0.39 g, 0.5 mmole) was dissolved in 3 ml of benzene and TCNE (0.064 g, 0.5 mmole) was added. The solution turned dark yellow and a small amount of solid formed. Methanol (20 ml) was then added, producing a 20% yield of the keteniminato-complex. The filtrate was warmed to 40-60° and evaporated to about 1/2 volume under reduced pressure. Addition of ca. 0.1 g of TCNE to this resulted in an immediate precipitation of 0.15 g of a light yellow solid. This was extracted with CH_2Cl_2, leaving a white residue whose infrared spectrum in the 1900-2500 cm^{-1} region was the same as that in d above. Anal. Found: C, 57.49; H, 3.05; N, 7.61; P, 6.79. mp (> 300°).

(b) To a solution of $Ir(C_6N_4H)(CO)(TCNE)(Ph_3P)_2$ (0.1 g) in CH_2Cl_2 was added 50 ml of methanol followed by reflux for 1 hr. A white product which formed at the high temperature was collected. Yield (0.03 g); mp (> 300°). Anal. Found: C, 57.98; H, 3.16; N, 7.63; mol wt, 950. Calcd for $C_{44}H_{30}IrN_5OP_2$: C, 58.80; H, 3.36; N, 7.79; P, 6.89; mol wt, 899.

(c) When 0.1 g of the keteniminato-complex was warmed at 50° for a few minutes with acetone and excess KCN and sufficient CH_2Cl_2 to bring the complex into solution, a dark reaction mixture resulted from which a white compound separated after the solution had stood overnight. The white product was collected and washed with water and

methanol. Yield, 0.08 g. The infrared spectrum in the 1900-2250 cm^{-1} region was identical to those samples as prepared above.

The triphenylarsine analogue of this compound was obtained by reacting $IrH_3(CO)(Ph_3As)_2$ (0.25 g, 0.3 mmole) and TCNE (0.154 g, 1.2 mmoles) in 20 ml of benzene at reflux temperature for 1 hr. The solid which formed in the hot solution was collected and washed with ethanol to give 0.25 g (84%) of $Ir(CN)(CO)(TCNE)(Ph_3As)_2$, mp 285° (dec). Anal. Calcd for $C_{44}H_{30}As_2IrN_5O$: C, 53.55; H, 3.06; N, 7.09. Found: C, 51.16; H, 2.83; N, 6.59.

(Cyano[benzyl]keteniminato)carbonyl(benzylidenemalonitrile)bis-(triphenylphosphine)iridium, $Ir(C_{10}H_7N_2)(CO)[C_6H_5CH=C(CN)_2](Ph_3P_2$. (Formulation tentatively assigned.)

a. The complex $IrH(CO)_2(Ph_3P)_2$ (0.39 g, 0.5 mmole) and $C_6H_5CH=C(CN)_2$ (0.39 g, 2.5 mmoles) were dissolved in 10 ml of benzene at room temperature with immediate darkening of the solution and evolution of CO gas. The solution was warmed to 45° for an hour and then evaporated to half volume under reduced pressure. The addition of 30 ml of MeOH produced a paler yellow solution followed in 15 min by the formation of a flocculent yellow precipitate. It was filtered, washed with MeOH and dried at 80° in vacuo. Yield, 0.45 g; mp 165°. Anal. Calcd for $C_{57}H_{43}IrN_4OP_2$: C, 64.94; H, 4.11; N, 5.22. Found: C, 65.05; H, 4.12; N, 5.14.

b. A small sample of $IrD(CO)_2(Ph_3P)_2$ was dissolved in CH_2Cl_2 and a five-fold excess of $C_6H_5CH=C(CN)_2$ was added. The solution was transferred to an ir cell and monitored for 2.5 hr after which time the reaction was complete. The ir pattern in the 1900-2250 cm^{-1} region was identical to that shown by the above product, indicating the absence of an Ir-H band in the compound.

The CH_2Cl_2 solution spectrum of the product in a, above, showed bands at 2195 w, 1985 vs, and 2127 s cm^{-1}. The first two bands were assigned to $\nu_{C\equiv N}$ and ν_{CO}, respectively, and the latter band was attributed to a ketenimine group, but the nmr spectrum of the compound was not consistent with the formulation assigned on the basis of ir. The nmr spectrum at 60 MHz and 100 MHz showed two doublets due to two different protons which were attributed to the banzyl protons in the keteniminato-ligand, but a peak slightly upfield and not of the correct intensity was not what was expected for a proton in the π-bonded moiety where splitting should be observed from coupling of this proton with the P atoms. The same product obtained in another preparation where hexane was used instead of MeOH as the precipitating agent exhibited the same type of nmr pattern, so MeOH was ruled out as a possible impurity.

c. The product from a (0.3 g) and 0.15 g of TCNE were stirred together in 15 ml of benzene at room temperature with darkening of the

yellow solution. Within five minutes, a precipitate formed which was collected and washed with benzene to yield 0.3 g of a dark green product. The Nujol mull spectrum of this crude product showed bands at 2068 vs, 2133 s, 2200 s, and 2228 m cm^{-1}, with the band at 2133 cm^{-1} attributed to the keteniminato-ligand. The product was recrystallized from CH_2Cl_2-benzene to yield yellow crystals with the same ir spectrum as the crude material. Anal. Calcd for $C_{53}H_{37}IrN_6OP_2$: C, 61.93; N, 8.17; H, 3.63. Found: C, 64.20; N, 6.94; H, 3.57. A second recrystallization gave an analysis; C, 63.48; N, 9.24; H, 3.59.

The nmr spectrum of this material showed the two doublets shifted slightly downfield, but also a single peak slightly downfield from them and of about the same intensity as that observed for the extra signal in the original product.

(Cyanoethyl)carbonyl(acrylonitrile)bis(triphenylphosphine)iridium, $Ir(C_3H_4N)(CO)(NCCH{=}CH_2)(Ph_3P)_2$.

The complex $IrH(CO)(Ph_3P)_3$ (0.5 g, 0.5 mmole) was added to 10 ml of acrylonitrile and the mixture was warmed to 50-60° whereupon solution occurred as the color lightened to pale yellow. After an hour of stirring, the solution was evaporated to about 1/2 volume, and 15 ml of hexane was added causing precipitation. The mixture was filtered and washed with hexane to yield 0.28 g of a white product. Anal. Calcd for $C_{43}H_{33}IrN_2OP_2$: C, 61.00; H, 3.90; N, 3.30; P, 7.31. Found: C, 60.22; H, 4.66; N, 3.62; P, 7.14.

The mull spectrum included bands at 2205 cm^{-1} and 1965 vs cm^{-1} which were assigned to $\nu_{C\equiv N}$ and ν_{CO}, respectively, on the basis of the

product formed from $IrD(CO)(Ph_3P)_3$ in the same manner and which showed the same ir bands.

The acrylonitrile adduct is unstable in solution, producing a yellow coloration, and attempts at crystallizing the crude material from a benzene-acrylonitrile mixture generally led to products exhibiting poor analyses. In further preparations of this adduct, wherein the product was allowed to crystallize from acrylonitrile, good analyses were obtained, but the ir spectrum was different for the carbonyl group in that it showed split bands at 1995 and 1985 cm^{-1}.

Reaction of $Ir(C_3H_4N)(CO)(NCCH{=}CH_2)(Ph_3P)_2$ with Fumaronitrile.

To 0.2 g of the complex in 5 ml of CH_2Cl_2 was added a solution of fumaronitrile in 5 ml CH_2Cl_2. The yellow solution was stirred for an hour at room temperature and then evaporated to 3-4 ml. The addition of 25 ml of MeOH caused the crystallization of 0.1 g of an off-white product, mp 165°. Anal. Calcd for $C_{43}H_{36}IrN_3OP_2$: C, 59.69; H, 4.20; N, 4.86. Found: C, 59.16; H, 3.95; N, 4.56.

Infrared bands were observed at 2218, 2205 sh, and 2036 vs cm^{-1}. The complex was not sufficiently soluble in $CDCl_3$ for nmr analysis and on standing, the solution turned dark yellow.

Complexes Derived from Acetylenes

Hydridobis(phenylethynl)carbonylbis(triphenylphosphine)iridium(III), $IrH(C{\equiv}CPh)_2(CO)(Ph_3P)_2$.

a. Three milliliters of phenylacetylene containing $IrH(CO)_2(Ph_3P)_2$ (0.39 g, 0.5 mmole) was warmed to 45-50° for 2 hr giving a dark brown solution. Addition of 30 ml of MeOH to the cooled solution precipitated 0.34 g (72%) of a beige solid which yielded white needles after two recrystallizations from CH_2Cl-MeOH. Yield, 0.23 g (49%), mp 180-185° (dec). Anal. Calcd for $C_{53}H_{41}IrOP_2$: C, 67.18; H, 4.36; mol wt, 947. Found: C, 67.01; H, 4.14; mol wt, 976.

The infrared spectrum in the 1900-2250 cm^{-1} region was identical for the crude and recrystallized material.

The above reaction was found to proceed to completion at room temperature in 2-3 days.

b. A good yield of the same product was obtained by heating $IrH(CO)(Ph_3P)_3$ in neat $PhC{\equiv}CH$ at 80-90° for 3 hr. The reaction mixture was monitored after heating at 50-60° for 0.5 hr and again after another hour by placing a drop of the solution between NaCl plates. The production and gradual disappearance of an intermediate with bands at 1970 and 2111 cm^{-1} was observed. The crude product exhibited an additional weak band at 2040 cm^{-1} and it was shown that a minor fraction with strong bands at 2045 and 2120 cm^{-1} could be separated from the main product by chromatographing on a silica gel column using a 2:1 volume

ratio of benzene-hexane as eluent. In view of the amount of material that would have to be chromatographed to obtain enough for an analysis and nmr study, a larger scale separation was not attempted.

(1,2-bis[trifluoromethyl]vinyl)carbonyl(hexafluorobutyne-2)bis-(triphenylphosphine)iridium, $Ir[C(CF_3)=CH(CF)_3](CO)[C(CF_3)\equiv C(CF_3)](Ph_3P)_2$.

Hexafluorobutyne was bubbled through a 70° solution of $IrH(CO)(Ph_3P)_3$ (0.5 g, 0.5 mmole) in 10 ml of benzene. The reaction mixture was taken to dryness and covered with EtOH-hexane to give a milky suspension and a yellow filtrate. The collected solid (0.3 g) was recrystallized from CH_2Cl_2-hexane and yielded a white product, mp 170°. Anal. Calcd for $C_{41}H_{31}F_6IrOP_2$: C, 50.50; H, 2.92; P, 5.78; F, 21.32; mol wt, 1069. Found: C, 50.24; H, 3.22; P, 5.80; F, 21.06.

The same compound was obtained in a similar manner from $IrH(CO)_2(Ph_3P)_2$.

Reaction of $IrH(CO)_2(Ph_3P)_2$ with Diphenylacetylene.

The iridium complex (0.77 g, 1 mmole) and PhC≡CPh (0.71 g, 4 mmoles) were heated together in 25 ml of benzene at 60-65° for 4 hr. The reaction mixture was evaporated to dryness and extracted with 20 ml of MeOH to remove the excess PhC≡CPH.. The residue was taken up in 10 ml of benzene, and 30 ml of MeOH was added. After sitting overnight in the cold, 0.6 g of a brown yellow solid formed. This was chromatographed on a silica gel column using benzene to remove a minor fraction which

exhibited a band at 1948-50 cm^{-1}. The main band was eluted with 50:50 benzene-methanol. The solvent was removed under reduced pressure and the yellow solid collected. Anal. Found: C, 63.23; H, 4.47; mp 138-140°; mol wt, 1054. Calcd for $IrH(CO)(Ph_3P)_2 \cdot 2PhC{\equiv}CPh$: C, 70.83; H, 4.66; mol wt, 1102.

The solution spectrum (CH_2Cl_2) of this product included bands at 2003 vs, 1617 s, 1586 s, 880 m, 873 m and 856 w cm^{-1}.

In two previous reactions, material with an infrared spectrum idientical to that above was obtained, but the carbon analyses were not consistent. The material exhibiting only the one band at 1948 cm^{-1} in the 1500-2250 cm^{-1} region varied in amounts in the three reactions and became a minor product if the length of time of heating was increased. This product was not further investigated.

The complex, $IrH(CO)(Ph_3P)_3$, did not react when heated at 60-65° with a five-fold excess of the acetylene in benzene. There were indications that a product was formed after several hours at reflux temperature, but attempts to isolate a characteristic product from the mixture were unsuccessful.

RESULTS AND DISCUSSION

Complexes Derived from Olefins

Fumaronitrile, cinnamonitrile, benzylidenemalononitrile, and fumaric acid in their reactions with one or more of the iridium substrates, $IrH(CO)(Ph_3P)_3$, $IrH(CO)_2(Ph_3P)_2$, and $IrH_3(CO)(Ph_3P)_2$ displace Ph_3P, CO, and H_2 respectively, at moderate temperatures (25-65°) to give complexes of the type, IrH(CO)(activated olefin)$(Ph_3P)_2$. The presence of the hydride ligand was established by deuteration studies and nmr where solubilities allowed. The presence of the hydride ligand in the fumaric acid complex was inferred from its infrared spectrum.

The olefins crotononitrile, 1,1-diphenylmethylenemalononitrile, and 1,2-diphenylmaleonitrile did not react with $IrH(CO)(Ph_3P)_3$ under the same preparative conditions, possibly for steric reasons for the latter two and lessened olefin activity for the former. The methyl group is considered to be more electron releasing than hydrogen and this effect in crotonitrile could partially negate the activating effect of the cyano group making this olefin unreactive compared to acrylonitrile which forms a di-olefin complex.

The infrared spectra of these cyanoolefin complexes are similar. Figure 2 shows the mull and solution spectra of one of these in the 1900-2250 cm^{-1} region. A common characteristic of these hydridocomplexes is the decreased intensity of the band due to the M-H stretching frequency relative to the bands for the cyano and carbonyl stretching frequencies in the solution spectra.

Selected band positions for the hydrido- and some of the corresponding deuterido-complexes are presented in Table I. Included are data for the fumaronitrile complex prepared from $IrH_3(CO)(Ph_3As)_2$.

A comparison of the data given in the table shows that there is a shift of 20-30 wavenumbers toward higher frequency for the carbonyl stretch in going from the hydrido- to the analogous deuterido-complexes and this is indicative of a trans arrangement for H and CO.

It is interesting to compare the ν_{Ir-H} and ν_{CO} values for the phosphine fumaronitrile complex with those for the arsine analogue. Triphenylarsine is a weaker π-acid and/or a better σ-donor than Ph_3P and this would lead to a higher electron density on the metal. The lower observed value for ν_{CO} in the arsine complex is in accord with the concept that increased electron density on the metal will result in increased back-donation to the π-antibonding orbitals of the CO resulting in a lower bond order. The metal-hydrogen stretching frequency was reported to be sensitive to the electron density on the metal[8] and this is borne out by the lower value for ν_{Ir-H} observed for the arsine complex.

A similar situation prevails for the cinnamonitrile complex in the phosphine series of hydrido-olefin complexes shown in the table. The lower values observed for ν_{Ir-H} and ν_{CO} for this complex could be interpreted as being due to reduced electron withdrawal from the metal by the olefin ligand through its π-system.

As noted in the Introductory section, an initial high electron density on the metal tends to favor the formation of stable olefin

Figure 2

Infrared Spectra of $IrH(CO)(NCCH{=}CHCN)(Ph_3P)_2$.

a. In HCBD mull

b. In CH_2Cl_2 solution

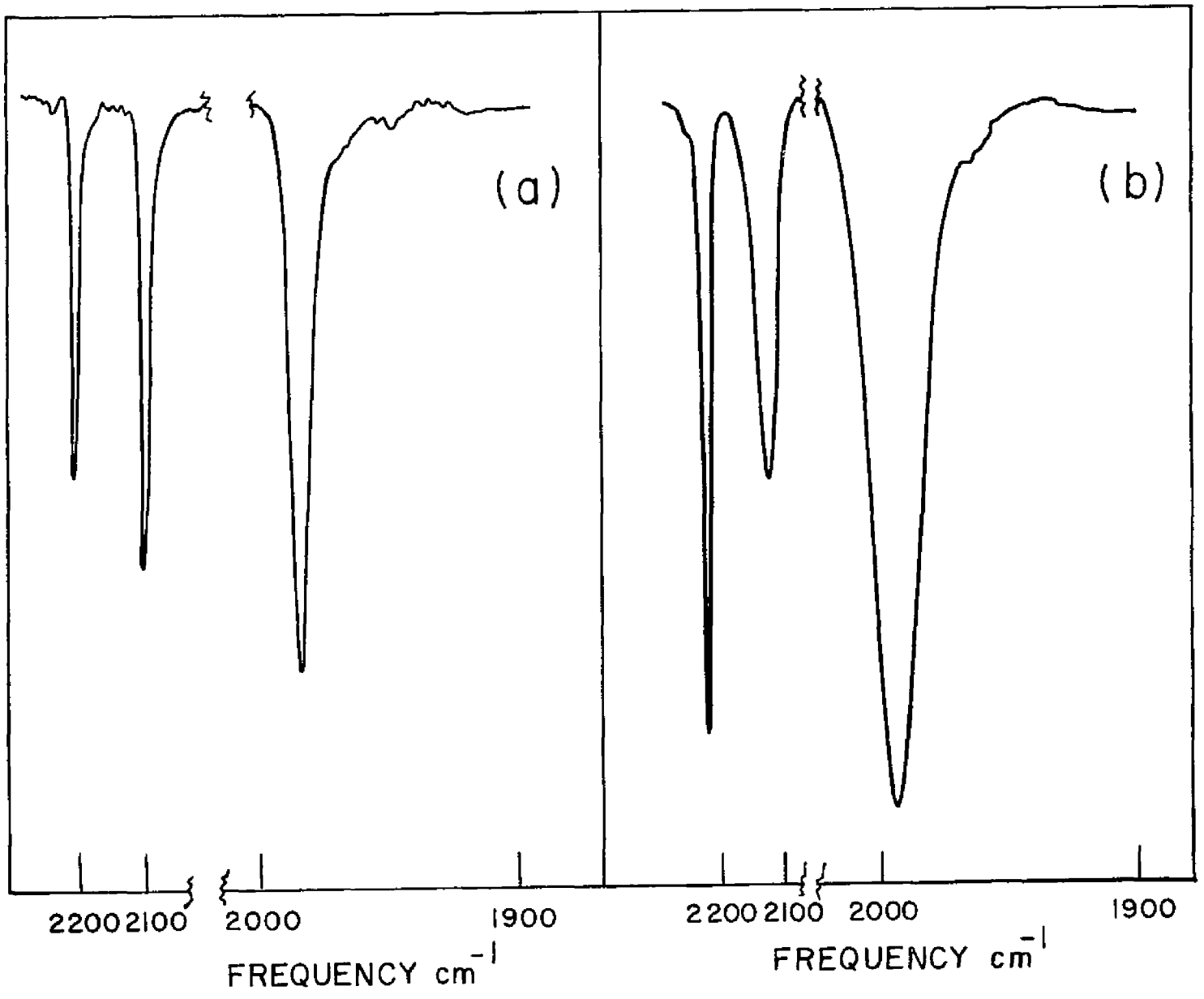

(a)
(b)
2200
2100
2000
1900
FREQUENCY cm⁻¹
2200
2100
2000
1900
FREQUENCY cm⁻¹

TABLE I

INFRARED STRETCHING FREQUENCIES[a] OF

HYDRIDO- AND DEUTERIDO-OLEFIN COMPLEXES[b]

Complex	ν_{CN}	ν_{Ir-H}	ν_{CO}	δ^{c}_{Ir-H}
$IrH(CO)(FUMN)L_2$	2215	2105	1987	830,855-865
	2211	2115	1995	817
$IrH(CO)(FUMN)L'_2$	2211	2080	1972	822,869
	2214	2094	1982	815,872
$IrD(CO)(FUMN)L_2$	2210		2021	
	2213		2023	
$IrH(CO)(CINN)L_2$	2210	2092	1963	870,888
	2208	2108	1974	900
$IrD(CO)(CINN)L_2$	2210		1985	
$IrH(CO)(BMN)L_2$	2213,2225sh	2108	1985,1995sh	807,819,889
	2220	2116	1992	820-830
$IrD(CO)(BMN)L_2$	2213, 2227sh		2019,2034sh	
	2221		2021	
$IrH(CO)(FUMA)L_2$		2123	1992	816,890-895

a. Band positions in cm^{-1}. HCBD mulls - first row values; CH_2Cl_2 solution - second row values.

b. Abbreviations used are: L = Ph_3P; L′ = Ph_3As; FUMN = fumaronitrile; CINN = cinnamonitrile; BMN = benzylidenemalononitrile; FUMA = fumaric acid.

c. These bands were all of weak intensity.

complexes. In an attempt to assess and/or confirm this factor, a series of olefin complexes was prepared from $IrCl(CO)(Ph_3As)_2$. The relative stabilities of these complexes as determined from preparative studies are presented in Table II where a comparison can be made with the hydrido-olefin complexes and olefin complexes derived from $IrCl(CO)(Ph_3P)_2$ which have been reported in the literature.[23] The greater stability of the hydrido-olefin complexes can be interpreted in terms of the hydride ligand being more electron releasing than chloride,[24] and for the arsine complexes, the Ph_3As ligand being a weaker π-acid and/or a better σ-donor than Ph_3P.

It would appear that the stabilities of the olefin complexes also depend on the extent to which they can withdraw this available electron density into their π-antibonding orbitals, leaving the metal atom with a more positive charge. If the ν_{CO} (or ν_{Ir-H}) values are used as an assessment of the positive charge on the metal atom, they should also give an indication of the relative stabilities of the olefin complexes in an analogous series. For the hydrido-complexes presented in Table I it is seen that the cinnamonitrile adduct should be the least stable which is the observed case. The cinnamonitrile ligand is readily displaced by fumaronitrile. The relative stabilities of the remaining phosphine-olefin complexes cannot be readily assessed from the infrared data, although fumaronitrile can replace the olefin ligand in these compounds as well to form the fumaronitrile adduct.

TABLE II

RELATIVE STABILITIES OF COMPLEXES OF THE TYPE $IrX(CO)(OLEFIN)L_2$

Olefin	X = Cl, L = Ph_3P[a]	X = Cl, L = Ph_3As[b]	X = H, L = Ph_3P[b]
Fumaronitrile	solid stable, dissociates slightly in solution	stable	stable
Acrylonitrile	solid dissociates	solid stable, dissociates in solution	complex not isolated[c]
Cinnamonitrile	no complex forms	complex not isolated, ir evidence for formation in solution	solid stable, decomposes slowly in solution
Benzylidenemalononitrile	no complex forms	solid stable, dissociates in solution	stable

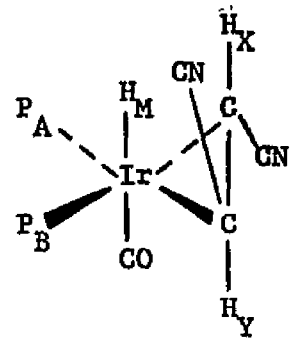
a.. Reference 23.

b. This work

c. The hydrido-olefin complex is assumed to be an intermediate in the formation of the di-olefin complex.

The value for ν_{Ir-H} in $IrH(CO)(NCCH{=}CHCN)(Ph_3As)_2$ given in Table I indicates that the M-H bond is weaker in this complex than in the analogous phosphine complex. The latter compound can be heated in the presence of excess fumaronitrile to 110° for an hour without change, but as noted in the Experimental section, the length of reaction time for the preparation of the former complex is critical. Two hours of heating at 80-90° produces a compound which does not contain an Ir-H bond but which, on the basis of nmr data, still possesses a bonded olefin. The starting material $IrH_3(CO)(Ph_3As)_2$, used for the preparation of the hydrido-olefin complex, is more stable than its corresponding phosphine analogue which underwent reactions with the olefins at moderate temperatures (50-60°). This stability, as pointed out in the Introductory section, can be attributed to the electron-donating properties of the arsine ligand which enhances the ability of d^8 complexes to undergo oxidative addition. Once the olefin complex is formed however, this same property of the arsine ligand apparently serves to weaken the M-H bond.

The structure of $IrH(CO)(NCCH{=}CHCN)(Ph_3P)_2$ has been deduced from a comparison with the infrared data of the corresponding deuteride-complex and has been confirmed by an X-ray single crystal analysis.[65] This complex exists in a trigonal bipyramidal configuration in the solid state as shown in V.



V

This is also the likely stereochemistry for the complex in solution based on the criterion of a shift in ν_{CO} and is the probable stereochemistry for all the hydrido-complexes prepared.

The nmr spectrum of the fumaronitrile adduct is characterized by "olefinic" proton absorptions in the 2-4 ppm range, i.e., values which are considerably further upfield than the resonance of the uncoordinated olefin (6.3 ppm). In the high field region, the hydride absorption pattern is centered at -11.27 ppm. This spectrum is consistent with a rigidly attached organic moiety bonded to the iridium with the stereochemistry being the same in solution as was found in the solid state by X-ray analysis. For such an arrangement, i.e., an "iridacyclopropane" structure, an ABMXY spectrum would be anticipated with nonequivalent phosphorus and hydrogen atoms labeled as in V.

The high field part of the spectrum was simplified by irradiating at 255 cps to remove the H_X and H_Y coupling to H_M. Figure 3 (a) shows the 250 Hz sweep width spectrum before (lower trace) and after decoupling (upper trace) where now the M part of the

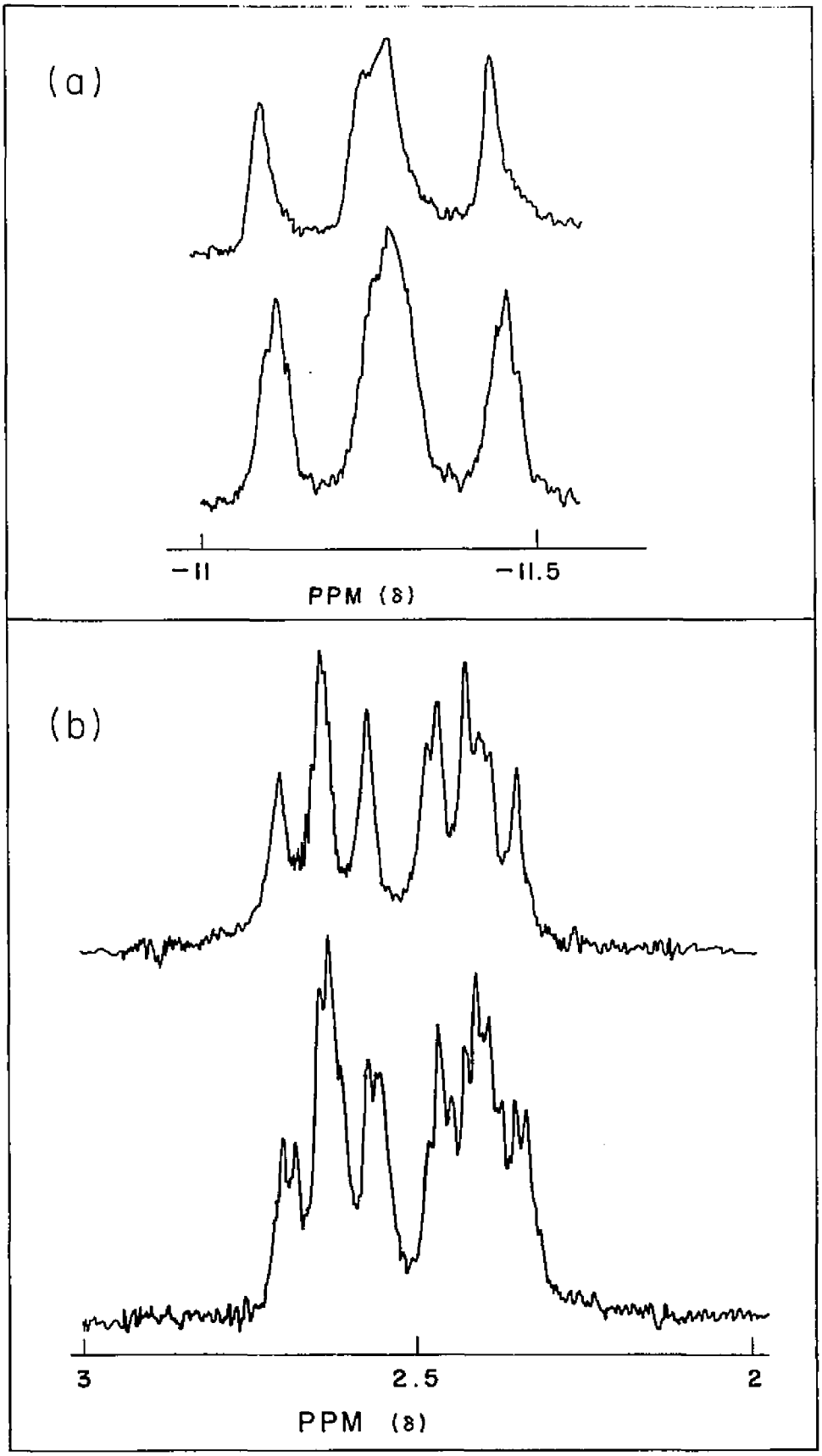
Figure 3

Proton Nuclear Magnetic Resonance Spectrum of

$IrH(CO)(NCCH{=}CHCN)(Ph_3P)_2$ at 100 MHz.

a. High Field Pattern

b. Low Field Pattern


(a)
−11
−11.5
PPM (δ)
(b)
3
2.5
2
PPM (δ)

ABM pattern has the outermost lines separated by the sum $J_{H_M-P_A} + J_{H_M-P_B}$ which is 34 Hz.

The low field portion of the spectrum is shown in Figure 3 (b). The upper trace is the ABXY pattern obtained after irradiation at -1127 cps to remove the H_M coupling. This pattern has not been completely resolved and no coupling constant for the olefinic hydrogens has been obtained.

A simpler pattern which shows the inequivalency of the olefinic protons was observed in the spectrum of IrCl(CO)(NCCH=CHCN)-$(Ph_3As)_2$. The AB pattern consists of two doublets centered at 2.84 and 3.20 ppm with $J_{Hx-Hy} = 8$ Hz. For this compound also, the spectrum is consistent with a rigidly attached organic moiety.

The AB part of the ABM pattern in the spectrum of the hydrido-analogue, IrH(CO)(NCCH=CHCN)$(Ph_3As)_2$, consists of 2 split doublets centered at 2.76 and 2.92 ppm. The high field pattern appears as a triplet centered at -11.76 ppm, which collapses to a singlet when irradiated at 285 cps. It was estimated that each member of the downfield doublets was split by ca. 1.5-2 Hz, which indicates the small coupling between the hydrido and olefinic protons. Irradiation of the highfield portion at -1176 cps produced a typical AB pattern with $J_{Hx-Hy} = 7$ Hz.

The point to be made here is that the magnitude of the coupling constants between the olefinic protons which were obtained from the spectra of the latter two complexes suggests that the olefin has lost its double bond character and is bonded to iridium to give a

"metallacyclopropane" structure depicted as in II. Whereas a range of values from 13-18 Hz have been reported[66] for the coupling between the trans hydrogen in -CH=CH- systems, lower values were observed for trans hydrogen coupling in cyclic structures, being 6.99 Hz[67] for bromocyclopropane and 5.58 Hz[68] for cyclopropane itself.

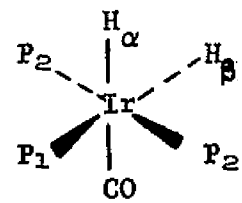
Low solubilities of the fumaric acid and cinnamonitrile complexes (the latter also tends to decompose in solution on standing) precluded nmr studies on these compounds. The nmr spectrum of the benzylidenemalononitrile complex attested to the presence of a mixture of isomers and the complex spectrum has not been resolved. The observed signals included a broad band centered at 3.8 ppm and a high field signal consisting of 7 separate split peaks centered at -10.34, -10.46, -10.54, -10.68, -10.80, -10.85, and -11.00 ppm.

The carboxyl-substituted olefins, maleic and cinnamic acid react with $IrH(CO)(Ph_3P)_3$ and $IrH(CO)_2(Ph_3P)_2$ to give the protonated cations $[IrH_2(CO)(Ph_3P)_3]^+$ and $[IrH_2(CO)_2(Ph_3P)_2]^+$, respectively. The former was first isolated by Malatesta[60] as the perchlorate salt and its structure was proposed by Vaska[57] on the basis of infrared data. Collman[63] isolated $[IrH_2(CO)_2(Ph_3P)_2]^+$ as the hexafluorophosphate salt and proposed the structure for this cation also on the basis of infrared data.

In this investigation, infrared and nmr spectra were obtained using CH_2Cl_2 solutions of the iridium substrates containing an excess of the acid. A summary of these experiments and results is presented in Table III. Only infrared bands additional to those already listed

in the Experimental section for the cations are given. For comparison, the infrared and high field nmr data are listed for the unprotonated species.

The nmr spectrum of $[IrH_2CO(Ph_3P)_3]^+$ is interpreted according to the correlation diagram shown in Figure 4. This 24-line spectrum is in accord with the stereochemistry as depicted in VI.



VI

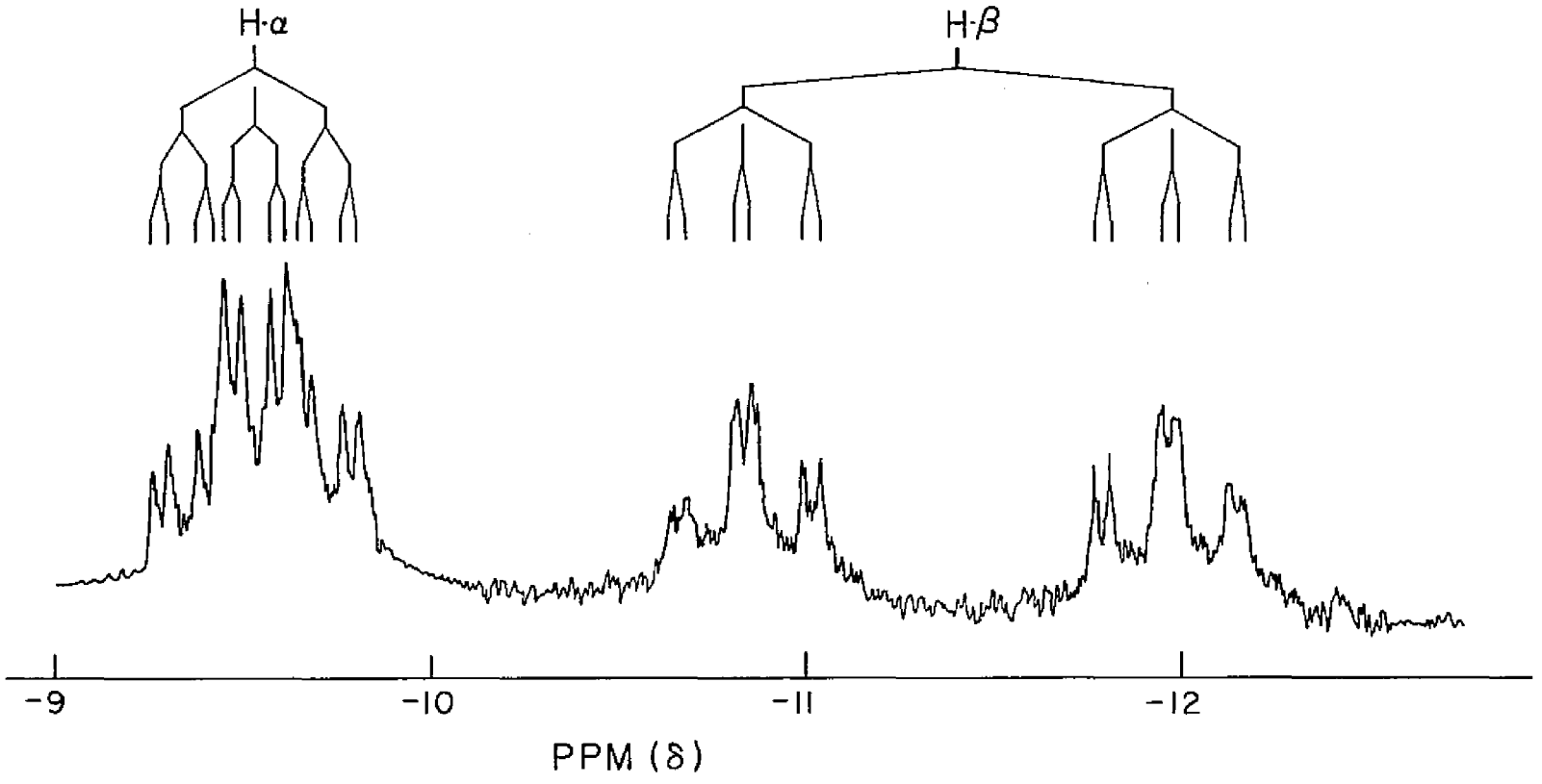
Coupling constants are: $J_{P_1-H_\alpha} = 12$; $J_{P_2-H_\alpha} = 19$; $J_{H_\alpha-H_\beta} = 4$; $J_{P_1-H_\beta} = 114$; $J_{P_2-H_\beta} = 18$ Hz; and the chemical shifts are: $H_\alpha = -9.53$; $H_\beta = -11.40$ ppm. These results corroborate the structure for the cation as proposed by Vaska. The sum, $J_{P_2-H_\alpha} + J_{P_1-H_\alpha} = 31$ is in good agreement with that found (34 Hz) for the cis-phosphorus couplings to the hydridic proton in the fumaronitrile complex.

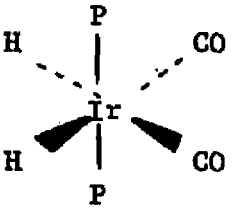
The cation $[IrH_2(CO)_2(Ph_3P)_2]^+$ exhibits a symmetric triplet centered at -10.0 ppm, $J_{P-H} = 15$ Hz. This indicates equivalency of phosphorus and hydrogen atoms and the stereochemistry as shown in VII.

Figure 4

Proton Nuclear Magnetic Resonance Spectrum of

$[IrH_2CO(Ph_3P)_3]^+$ at 100 MHz.


H·α
H·β
-9
-10
-11
-12
PPM (δ)



VII

An equally probable <u>trans</u> arrangement of the hydrogen atoms was ruled out on the basis of the infrared data and the above structure is in agreement with that proposed by Collman.

The results summarized in Table III show that maleic acid in the concentration used reacts almost completely with both of the iridium substrates in CH_2Cl_2 as solvent. No unprotonated form nor π-bonded form was detectable by infrared or nmr.

Cinnamic acid in the concentration used does not completely protonate $IrH(CO)_2(Ph_3P)_2$. The unprotonated species was detectable with infrared and nmr. The broadening and shifting to lower frequency of the CO bands in the starting material may be due to the high concentration of the acid present. Cinnamic acid does not fully protonate $IrH(CO)(Ph_3P)_3$ and an additional broad weak band at 1965 cm^{-1} was observed in the infrared spectrum. This was attributed to the unprotonated species since the yellow color due to the starting material in the solution was not completely discharged on the addition of this acid as was the case for maleic acid. Although no nmr evidence was obtained for the presence of some unprotonated species since its resonance

TABLE III

INFRARED AND NMR DATA ON CH_2Cl_2 SOLUTIONS OF HYDRIDOIRIDIUM

COMPLEXES CONTAINING MALEIC OR CINNAMIC ACID

Substrate	Acid	Molar Ratio Substrate:Acid	IR[a]	NMR PPM	J(Hz)
$IrH(CO)(Ph_3P)_3$			2070w,1930vs[b]	-11.2q	42[c]
	maleic	< 1:2		- 9.53m[d]	
				-10.85t	
				-11.98t	
	cinnamic	1:5	1965br,w		
$IrH(CO)_2(Ph_3P)_2$			2095w,2060sh	-11.3t	3[e]
			1990s,1979m		
			1933sh,1927s[b]		
	maleic	< 1:2		-10.0t	15
	cinnamic	1:8	2015w,1964-70br,s,	-10.0t	15
			1920-23br,s	-11.3t	3

a. Only bands additional to those of the protonated species are given.

b. Solution of the substrate only

c. Reference 51. q = quartet; m = multiplet; t = triplet

d. Spectrum shown in Figure IV; coupling constants given on p. 57

e. Reference 55.

signals would overlap with that of the cationic species, indirect evidence that the band at 1965 cm^{-1} is not due to a π-bonded species came from the infrared monitoring of a benzene solution of $IrH(CO)(Ph_3P)_3$ and cinnamic acid warmed to 40-50° for an hour. In this solvent, no cationic species was formed and only bands due to the starting material were observed.

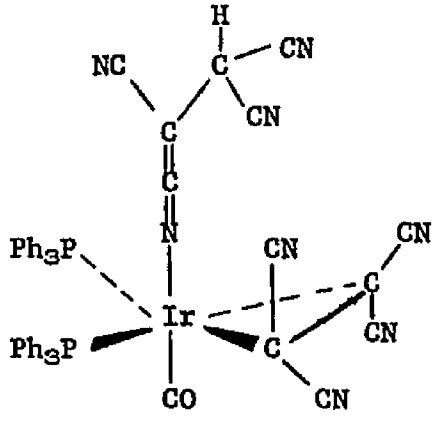
Fumaric acid, on the other hand, does produce a mixture of the protonated cation and a π-bonded complex which is easily isolated because of its insolubility in polar and nonpolar solvents.

In summary then, maleic acid stabilizes $IrH(CO)(Ph_3P)_3$ as the cation so that elimination of Ph_3P and π-bond formation is not favored. Cinnamic acid apparently is not activated sufficiently as an olefin to π-bond, even though it does not fully protonate the iridium substrate. Fumaric acid, less able to protonate than maleic acid, is activated enough as an olefin to π-bond.

The complex (Cyano[dicyanomethyl]keteniminato)carbonyl(tetracyanoethylene)bis(triphenylphosphine)iridium.can be formed by the action of TCNE on $IrH(CO)_2(Ph_3P)_2$, $IrH(CO)(Ph_3P)_3$ or $IrH_3(CO)(Ph_3P)_2$ although the yields vary. The first iridium substrate gives a good yield of the complex in a clean reaction in a benzene solution. The use of $IrH(CO)(Ph_3P)_3$ is complicated by a reaction between TCNE and the displaced Ph_3P ligand leading to tar formation. As pointed out in the Experimental section, the addition of alcohol to the benzene reaction mixture gives a higher yield, but the product is quite impure.

The trihydridoiridium substrate does not readily react at room temperature and the reaction mixture must be warmed to 45-50°. In this one experiment, ethanol was added to precipitate a 10% yield of the complex, so it is not known whether prolonged heating of the benzene solution of the reactants would produce more of the complex or whether $Ir(CN)(CO)(TCNE)(Ph_3P)_2$ would be produced as is the case for the arsine analogue of the trihydrido-iridium substrate (vide infra).

The structure of $Ir(C_6N_4H)(CO)(TCNE)(Ph_3P)_2$ was proposed on the basis of elemental analysis, and infrared and nmr spectral data. It has been confirmed by a single crystal X-ray analysis[64] which shows a trigonal bipyramidal configuration about the iridium atom with the two P atoms and the TCNE in the equatorial plane, depicted as in VIII. The Ir-N-C angle was reported as 162°.



VIII

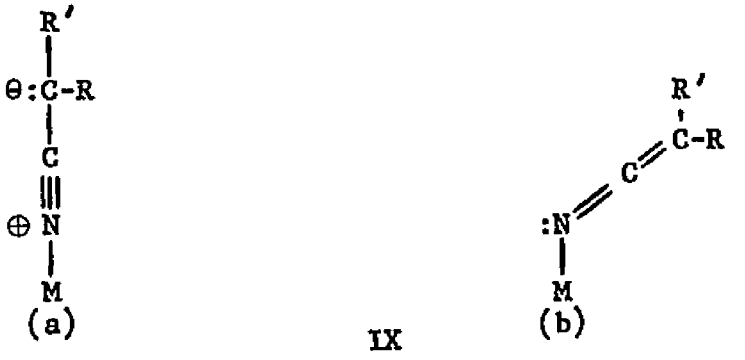
Selected ir band positions for this complex were assigned on the basis of similar values reported in the literature[33] and are as follows:

ν_{CN}	$\nu_{N=C=C(asym)}$	ν_{CO}	$\nu_{N=C=C(sym)}$	
2233sh,2220s	2168vs	2080vs	1360w	(CH_2Cl_2)
2233m,2209s	2158vs	2075vs	1355w	(HCBD)

The mull and solution spectra in the 1950-2250 cm^{-1} region given in Figure V show that the intensity of the band due to the ketenimine group is not markedly different in the two media in contrast to a band due to Ir-H as pointed out earlier. This effect has been useful in predicting whether or not a band in this region is due to ν_{Ir-H}.

The nmr spectrum is consistent with the above formulation, and shows a singlet at 4.2 ppm whose integrated intensity is ca. 1/30 that of the phenyl protons.

The reported bond angle for Ir-N-C of 162° would suggest that N is sp hybridized with a distortion from linearity due to the bulky Ph_3P groups rather than a distortion from 120° for an sp^2 hybridized atom. Thus, a resonance structure such as IX (a) would be considered a more important contributing form than IX (b).



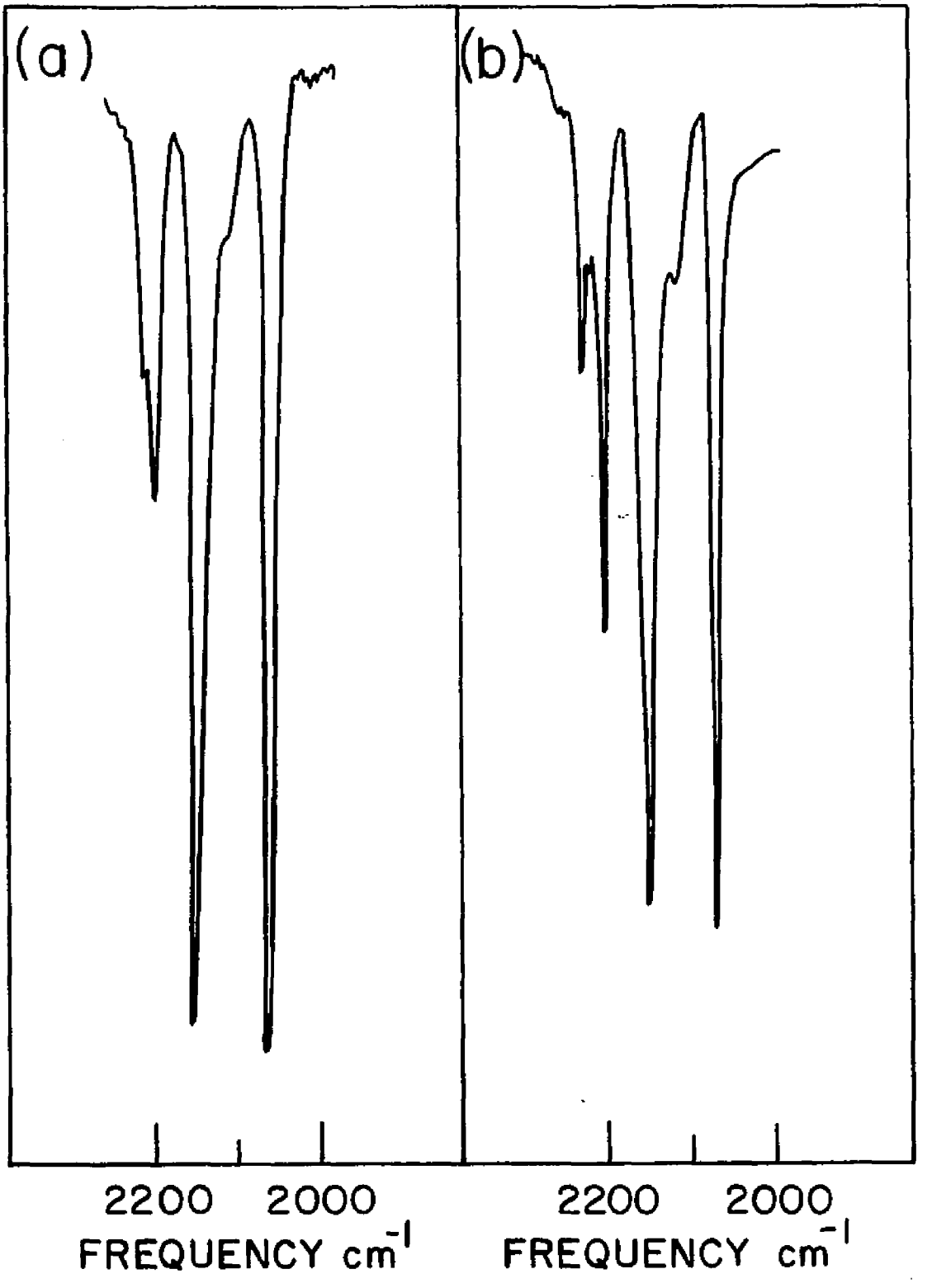
IX

Figure 5

Infrared Spectra of $Ir(C_6N_4H)(CO)[C(CN)_2=C(CN)_2](Ph_3P)_2$.

a. In CH_2Cl solution

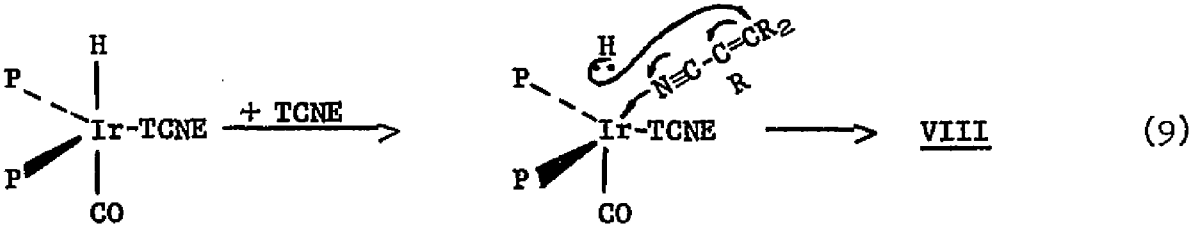
b. In HCBD mull


(a)
(b)
2200
2000
FREQUENCY cm⁻¹
2200
2000
FREQUENCY cm⁻¹

If the value of 2080 cm^{-1} for ν_{CO} in this complex is compared to the range of values[23] of 2055-2065 cm^{-1} for ν_{CO} in $IrX(CO)(TCNE)(Ph_3P)_2$ (X = Cl, Br, I, NCO, NCS) it would appear that the keteniminato-ligand is not only less electron-releasing than X, but rather electron-withdrawing, and this effect would be consistent with canonical form IX (a) which depicts a partial positive charge on the N atom bonded to the iridium.

Speculation regarding possible reaction pathways leading to the formation of the keteniminato-complex leads to several possible mechanisms:

(a) A hydrido-π-olefin complex is first formed followed by nucleophilic attack by the nitrile nitrogen of a second TCNE molecule to give a 1,4-addition in a 6-center concerted reaction.



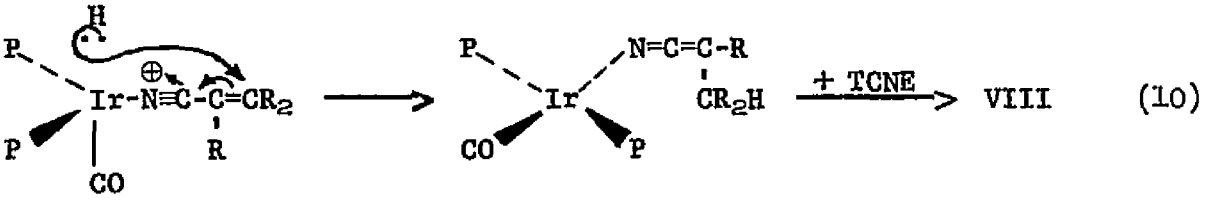
(9)

R = CN

If the π-bonded TCNE moiety removed sufficient electron density from the metal to invite nucleophilic attack, then the resulting increase in electron density from the nitrile nitrogen might serve to weaken the Ir-H bond and 1,4-addition would follow as depicted in eq. 9. However, no reaction was found to occur between TCNE and the hydrido-fumaronitrile complex at moderate temperatures although in view of the

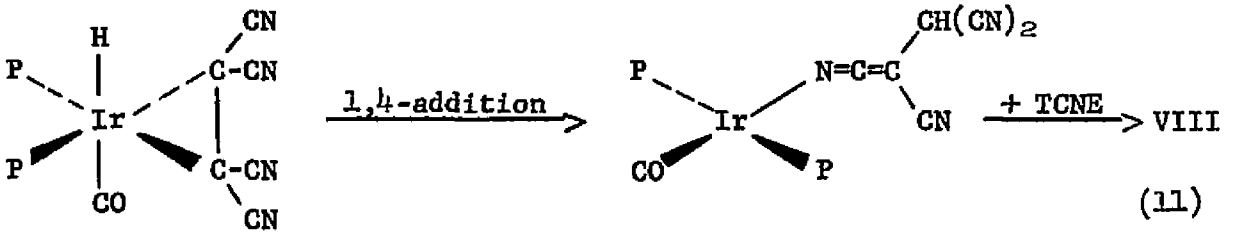
rather high value for ν_{CO} in this complex, one might predict that the metal would be sufficiently positively charged to be open to nucleophilic attack. The lack of reaction in this case may constitute evidence against such a mechanism.

(b) Tetracyanoethylene displaces either a CO or a Ph_3P ligand from the appropriate iridium substrate by approaching N end-on. The resulting increase of electron density on the iridium atom would lead to a weakening of the Ir-H bond and hydrogen transfers as in (a) to give 1,4-addition. This unsaturated iridium(I) complex then adds a second olefin.



(10)

(c) A hydrido-π-olefin complex is formed initially, followed by a 1,4-addition to the coordinated TCNE to give a coordinatively unsaturated iridium(I) complex which subsequently adds a second molecule of the olefin.



(11)

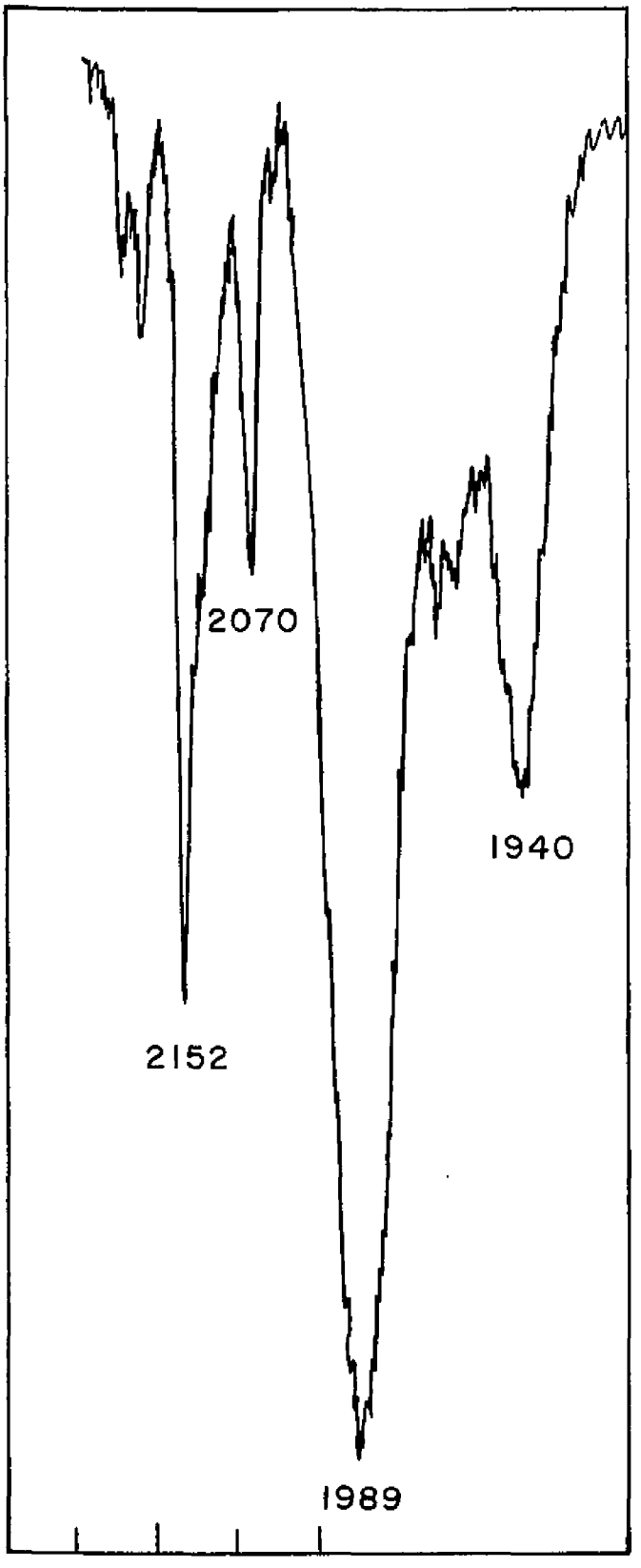
Molecular orbital calculations[89] indicate that there is a build-up of negative charge on the nitrile nitrogens relative to the carbon atoms in TCNE and it may be possible for hydride transfer to take place, followed by an internal electrophilic attack by the iridium on one of the nitrogen atoms to complete the 1,4-addition.

Qualitative evidence in favor of either pathway (b) or (c) comes from infrared monitoring of a reaction mixture of $IrH(CO)_2(Ph_3P)_2$ and TCNE. The spectrum of the mixture given in Figure 6 shows that the band at 2152 cm^{-1} is more intense than the carbonyl band at 2070 cm^{-1}, whereas they are about equally intense in the final product (see Figure 5). Also shown in Figure 6 are the two lower frequency bands due to carbonyl in the starting material, one of which (1940 cm^{-1}) has decreased in intensity due to its replacement and the other (1989 cm^{-1}) which has not undergone any shift in frequency from its original position. This spectrum is consistent with the formation from the dicarbonyl complex of VIII and $Ir(C_6N_4H)(CO)(Ph_3P)_2$ with the latter intermediate complex in higher concentration. This suggests that this intermediate is a precursor to VIII.

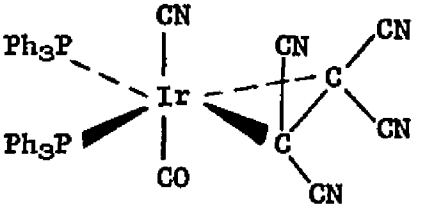
The white compound described in the Experimental section as a by-product fromed when alcohol was used during the trial preparations of the keteniminato-complex (VIII), has been formulated as $Ir(CN)(CO)(TCNE)(Ph_3P)_2$, consistent with the elemental analysis which indicates a P:N atom ratio of 2:5. Structure X is suggested.

Figure 6

Infrared Spectrum of a Reaction Mixture Containing a 1:1 Molar Ratio of TCNE:$IrH(CO)_2(Ph_3P)_2$ in Benzene.



Frequency cm^{-1}



X

The mull and solution spectra for this compound and the mull spectrum for the arsine analogue in the 2000-2250 cm^{-1} region are shown in Figure 7. These spectra are very similar to those reported for $IrX(CO)(TCNE)(Ph_3P)_2$ (X = Cl, Br, I, NCO, NCS) where geometrical isomerism was invoked to explain the lower frequency band which was not observed in the solution spectrum since isomerization to the more stable isomer had taken place.[23] The bands at 2080 and 2232 cm^{-1} (Figure 7. (a)) are probably ν_{CO} and ν_{CN} (of TCNE) respectively by comparison with these aforementioned complexes. It is probable that the band due to the cyano-ligand attached to the iridium overlaps with the band at 2230 cm^{-1} due to the cyano groups in TCNE since this band showed either a slight splitting or a shoulder in the various spectra that were examined.

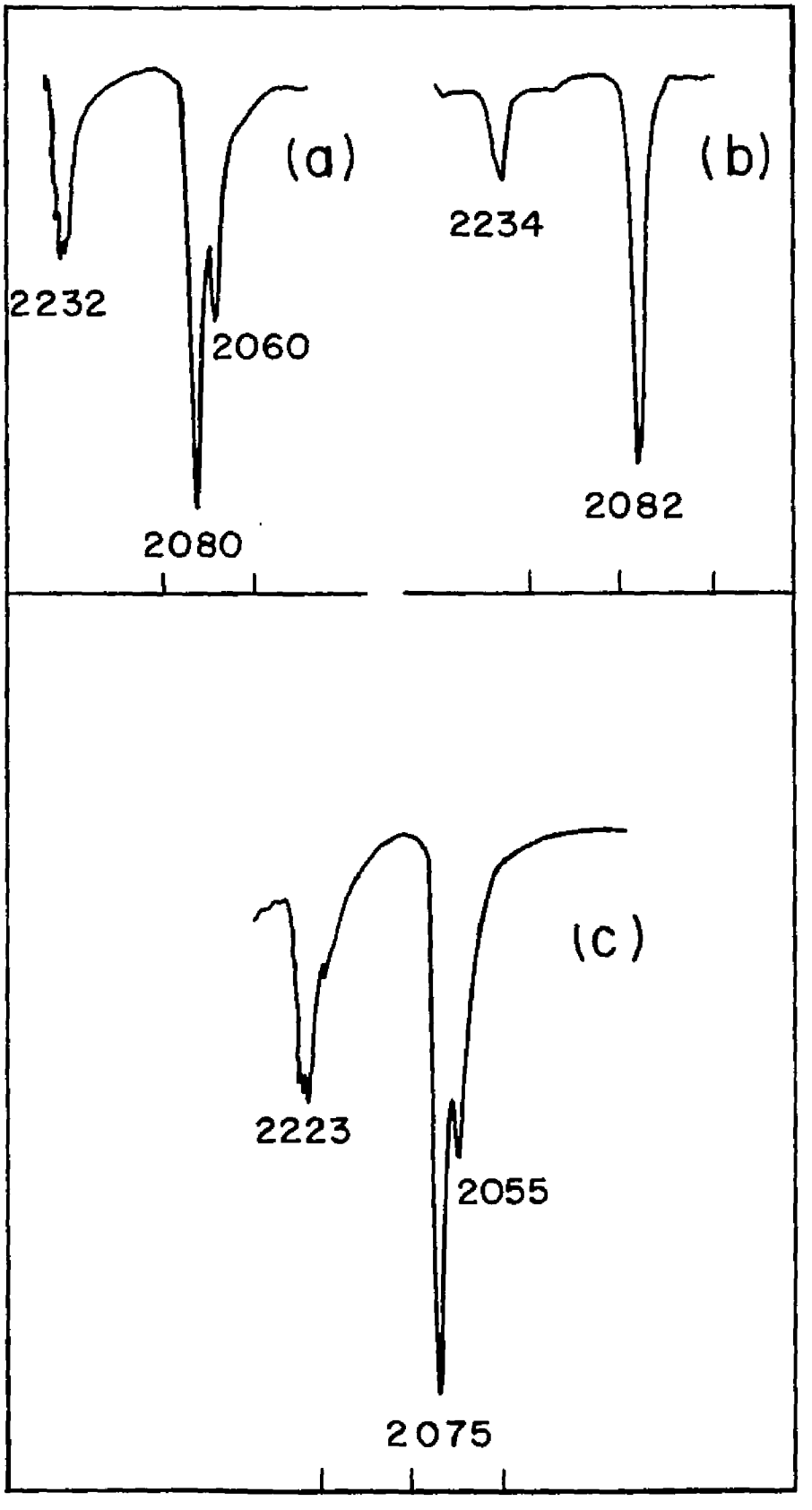
Further evidence for the formulation of the white product as X comes from the other methods of preparation of the compound. When VIII is warmed with KCN in acetone, the keteniminato-ligand is displaced by cyanide ion, analogous to the displacement reactions undergone by stannylketenimines with reactive halides (eq. 8). When VIII is refluxed in methanol, a low yield of X is obtained. A

Figure 7

a. Infrared Spectrum of $Ir(CN)(CO)(TCNE)(Ph_3P)_2$ in Nujol mull.

b. Infrared Spectrum of $Ir(CN)(CO)(TCNE)(Ph_3P)_2$ in CH_2Cl_2 solution.

c. Infrared Spectrum of $Ir(CN)(CO)(TCNE)(Ph_3As)_2$ in Nujol mull.


(a)
2232
2060
2080
(b)
2234
2082
(c)
2223
2055
2075
Frequency cm⁻¹

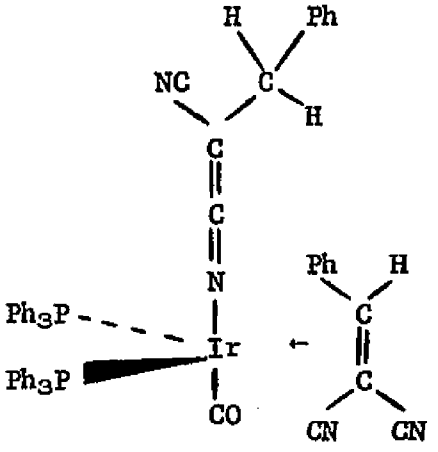
reasonable reaction path would involve the formation of an iridium alkoxide intermediate (analogous to the formation of stannyl alkoxides by alcoholysis of stannylketenimines according to eq. 7) which could then undergo nucleophilic displacement by the cyanide ion generated in solution by the action of alcohol on the cleaved keteniminato-moiety.

When TCNE and $IrH_3(CO)(Ph_3As)_2$ are refluxed together in benzene, the triphenylarsine analogue of X precipitates from the hot solution. No reaction occurs when these reactants are warmed in benzene at 50-60°, in contrast to the reaction between TCNE and $IrH_3(CO)(Ph_3P)_2$. It may be that the triphenylarsine analogue of VIII is formed as an intermediate which is unstable in refluxing benzene and decomposes to $Ir(CN)(CO)(TCNE)(Ph_3As)_2$.

It was hoped to synthesize X from $Ir(CN)(CO)(Ph_3P)_2$ and TCNE for final evidence, but attempts to form $Ir(CN)(CO)(Ph_3P)_2$ from the chloro-analogue (Vaska's compound) by a metathetical reaction were unsuccessful.

The high value for ν_{CO} shown in Figure 7 (a) is to be expected in view of the π-acceptor character of the cyanide ion which is comparable in its electron-withdrawing ability to that of the keteniminato-ligand. The lower observed value for ν_{CO} in the triphenylarsine analogue (Figure 7 (c)) is in keeping with the weaker π-acidity of the triphenylarsine ligand.

The elemental analysis and infrared spectral data for the product of the reaction between $IrH(CO)_2(Ph_3P)_2$ and $C_6H_5CH{=}C(CN)_2$ best fit the following formulation:



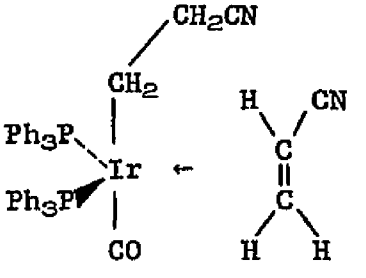
XI

A compound analogous to XI with an identical infrared spectrum in the 1900-2250 cm^{-1} region is obtained when the deuteridoiridium complex is employed. The nmr spectrum of XI exhibits no high field signal indicating the absence of a hydrogen bonded to iridium. The spectrum does show two low field doublets consistent with the two benzyl protons in the keteniminato-moiety but an extra signal in the spectrum has not been interpreted as due to the proton in the π-bonded moiety. Attempts to replace this group with TCNE to produce a simplified spectrum have not given a definitive answer. Successive recrystallizations of this substitution product apparently cause the compound to undergo change as evidenced by the inconsistent elemental analyses.

Benzylidenemalononitrile does form a keteniminato-complex when it reacts with $HPb(C_4H_9)_3$[34] which suggests that the formulation given in XI is entirely possible.

It is of interest that $C_6H_5CH{=}C(CN)_2$ reacts differently with $IrH(CO)_2(Ph_3P)_2$ and $IrH(CO)(Ph_3P)_3$, forming a hydrido-monoolefin complex with the latter iridium substrate. This is in contrast to the other activated olefins employed in this study which react to form identical products regardless of the iridium substrate used. The reason for the anomalous behavior of benzylidenemalononitrile is not understood but it is surely a problem for further study.

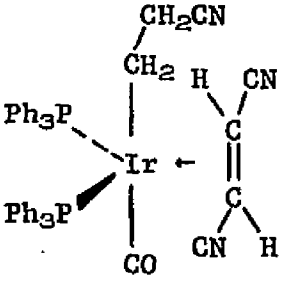
On the basis of the elemental analysis, the product from the reaction of acrylonitrile and $IrH(CO)(Ph_3P)_3$ has been formulated as $Ir(C_3H_4N)(CO)(NCCH{=}CH_2)(Ph_3P)_2$. Structure XII is proposed.



XII

It is suggested that a hydrido-olefinic complex is initially formed followed by "insertion" of the olefin into the Ir-H bond to produce the four coordinate σ-cyanoethyl complex which then adds a second olefin molecule to form the resultant complex. If the hydride ligand is considered anionic in nature, then the σ-bonded group would be expected to be bonded to iridium to produce an Ir-$CH(CH_3)CN$ linkage during the insertion step.[39] However, the presence on the metal of ligands of high π-acidity can increase the polarity of the M-H bond in the direction of $M^{\delta-} - H^{\delta+}$[66] and so favor the type of insertion depicted as in XII for the σ-bonded moiety.

Further evidence in favor of formulation XII comes from the reaction of the complex with fumaronitrile in which it is assumed that the π-bonded moiety has been replaced to give XIII.



XIII

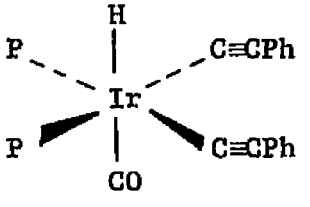
The carbonyl stretching frequency increases from 1965 cm^{-1} to 2036 cm^{-1} when fumaronitrile replaces acrylonitrile. This suggests that the σ-bonded cyanoethyl moiety is less electron-releasing than hydrogen since the ν_{CO} bond in the hydridofumaronitrile complex occurs at 1987 cm^{-1}.

Complexes Derived from Acetylenes

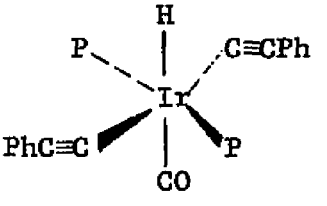
When PhC≡CH is heated with either $IrH(CO)(Ph_3P)_3$ or $IrH(CO)_2(Ph_3P)_2$, a white complex is obtained which has been formulated as a diacetylide on the basis of ir, nmr and elemental analysis.

Figure 8 shows the mull spectrum in the region 1900-2250 cm^{-1}. The bands are assigned as follows: 2009 vs (ν_{CO}); 2140 m (ν_{Ir-H}); and 2125 vs ($\nu_{C\equiv C}$) cm^{-1}. The latter intense band is characteristic of a σ-bonded acetylide group.[47] In the 800-900 cm^{-1} region, medium bands at 820 and 867 are assigned to δ_{Ir-H}.

The nmr spectrum of a saturated solution of the compound in CD_2Cl_2 at 60 MHz shows multiplets centered at 6.4, 6.9, 7.4, and 7.8 ppm due to phenyl protons and a high field symmetrical triplet centered at -9.2 ppm (J_{P-H} = 15 Hz), whose integrated intensity is 1/40 that of the phenyl protons. A symmetric triplet is consistent with either of the following two structures wherein the P atoms are equivalent.



(a)

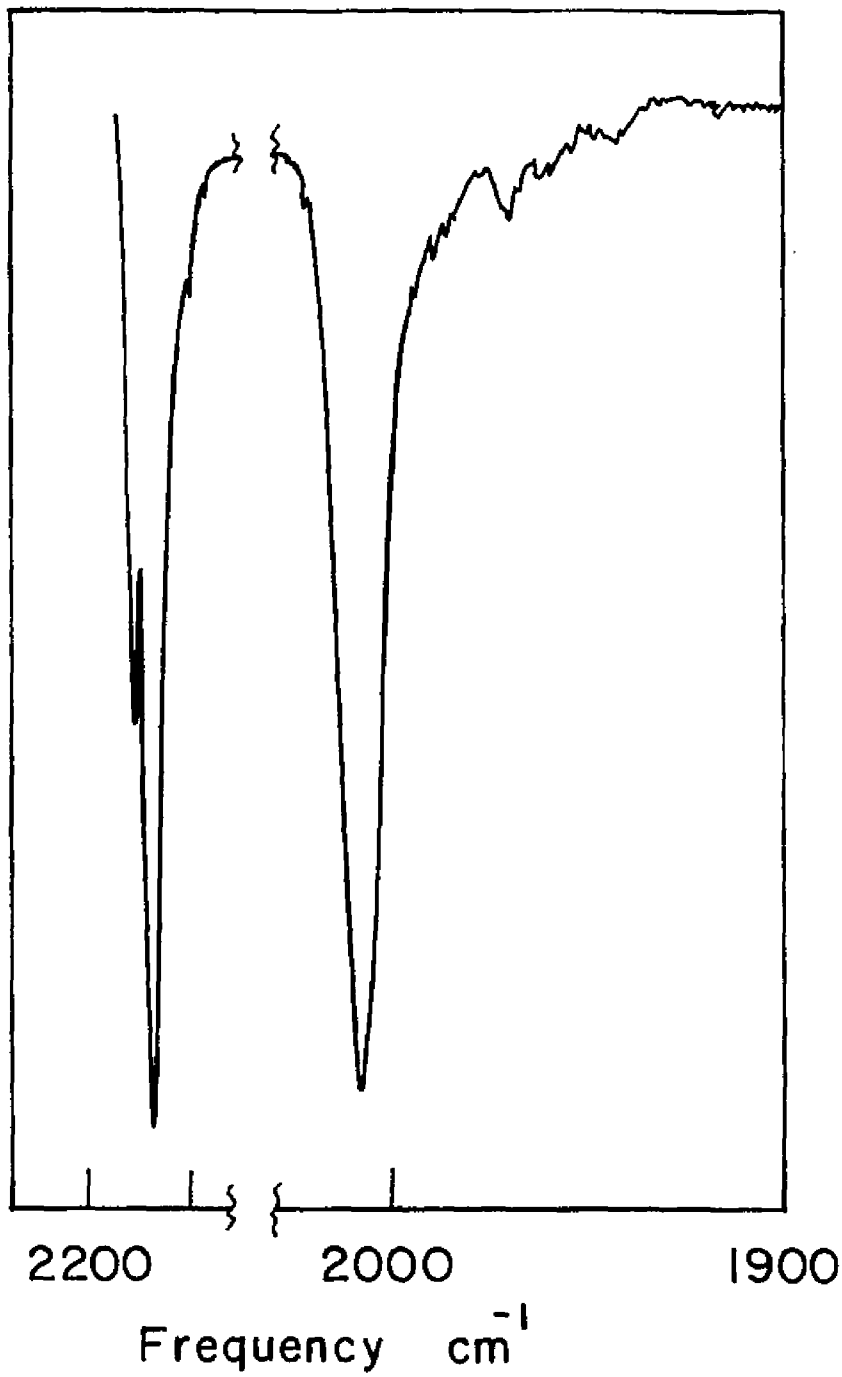


(b)

XIV

Figure 8

Infrared Spectrum of $IrH(C{\equiv}CPh)_2(CO)(Ph_3P)_2$ in Nujol Mull.


2200
2000
1900
Frequency cm⁻¹

On the basis of the one intense band at 2125 cm^{-1}, the trans structure is favored. Structure XIV (a) would be expected to show two $\nu_{C\equiv C}$ bands.

Brown and Wilkinson reported in a recent paper[71] that alk-1-ynes react with $IrH(CO)(Ph_3P)_3$ and $IrH(CO)_2(Ph_3P)_2$ by displacement of Ph_3P and CO respectively, to give the intermediate $[Ir(C\equiv CR)H_2(CO)(Ph_3P)_2]$. This cis-dihydrido-complex readily loses hydrogen and iridium(I) acetylide complexes of stoichiometry $Ir(C\equiv CR)(CO)(Ph_3P)_2$ or 3 are formed according to eq. 12.

$$[Ir(C\equiv CR)H_2(CO)(Ph_3P)_2] \xrightarrow[(+Ph_3P)]{-H_2} Ir(C\equiv CR)(CO)(Ph_3P)_2 \text{ or } 3 \qquad (12)$$

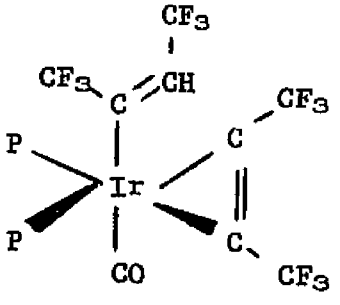
These complexes were reported to react with an excess of alk-1-ynes to give orange solutions. The orange-yellow square complexes undergo a wide range of oxidative-addition reactions and readily add oxygen even in the solid state. The yellow five-coordinate complexes establish the following equilibrium in solution:

$$Ir(C\equiv CR)(CO)(Ph_3P)_3 \rightleftarrows Ir(C\equiv CR)(CO)(Ph_3P)_2 + Ph_3P \qquad (13)$$

The mechanism for the addition of $PhC\equiv CH$ to the iridium substrates is postulated to proceed in the same manner as for the addition of alk-1-ynes. However, in contrast to alk-1-ynes, a second molecule of $PhC\equiv CH$ can add to the square planar complex to produce $IrH(C\equiv CPh)_2(CO)(Ph_3P)_2$.

The reaction between PhC≡CH and $IrH(CO)_2(Ph_3P)_2$ proceeds to completion at 50-60° in less than 2 hr although the reaction can occur at room temperature over a longer period of time. When the same diacetylide is prepared from $IrH(CO)(Ph_3P)_3$, a yellow intermediate first forms at 50-60° and the reaction mixture requires heating at 80-90° for 3 hr to convert this intermediate completely to the end product. It is suggested that the displaced Ph_3P competes with PhC≡CH in a faster reaction with the square planar complex to produce $Ir(C{\equiv}CPh)(CO)(Ph_3P)_3$ which then must dissociate before PhC≡CH can react to produce the more stable diacetylide.

The structure of the complex formed from the reaction of $CF_3C{\equiv}CCF_3$ with either $IrH(CO)(Ph_3P)_3$ or $IrH(CO)_2(Ph_3P)_2$ has been formulated as a σ-vinyl, π-acetylene compound (XV) on the basis of ir and elemental analysis. The complex is sparingly soluble in $CDCl_3$ and CD_2Cl_2, and no nmr spectrum was obtained.



XV

The Nujol mull spectrum includes bands at 1991 vs (ν_{CO}), 1742 s ($\nu_{C\equiv C}$), and 1610 m ($\nu_{C=C}$) cm^{-1}. Two additional medium intensity bands located at 2003 and 825 cm^{-1} are not considered as due to ν_{Ir-H}, although this has not been confirmed by preparing the analogous deuterium compound. The low frequency band has been assigned to $\nu_{-C=CH-}$ which can occur as a strong band in the 800-840 cm^{-1} region.[50] The band at 2003 cm^{-1} is low for ν_{Ir-H} in these types of complexes and is likely indicative of geometrical isomerism.

The strong band at 1742 cm^{-1} is characteristic of a strongly bound π-acetylene wherein the triple bond stretching frequency has been lowered considerably from the range 2260-2190 cm^{-1}, normally exhibited[50] by disubstituted acetylenes. A similar absorption was reported[27] at 1773 cm^{-1} for the hexafluorobutyne-2 in $IrCl(CO)(CF_3-C\equiv C-CF_3)(Ph_3P)_2$, and it was implied that the coordinated acetylene exhibits strong angular distortion and is doubly σ-bonded to the metal atom.

A mechanism which suggests itself is initial π-bond formation with the hydrido-substrate followed by insertion of the acetylene into the M-H bond to give the σ-vinyl derivative which then π-bonds with another acetylene molecule. This process may be operative in the linear polymerization of acetylenes catalyzed by transition metals,[43] and for that reason the above compound is of interest in that it is one of the first examples wherein a species analogous to an intermediate has been isolated.

No formulation has been arrived at for the product obtained from the reaction of diphenylacetylene with $IrH(CO)_2(Ph_3P)_2$ as described in the Experimental section. The molecular weight indicates a 2:1 ratio for the acetylene:iridium, but analyses have not been consistent and further chromatographic procedures using various solvent systems may indicate that the product is non-homogeneous.

A tentative formulation would be similar to that shown for XV, which would account for the strong bands at 1617 and 1586 in the ir in the double bond region and in the 800-900 cm^{-1} region. However, this would require an overlapping of $\nu_{C\equiv C}$ with ν_{CO} at 2003 cm^{-1}. The nmr spectrum is inconsistent in that it shows in addition to the phenyl protons, two complex multiplets centered at 3.5 and 4.5 ppm.

CONCLUDING STATEMENTS

This research has resulted in the preparation of several stable hydrido-olefin complexes of iridium. These complexes are the first of their type that have been well characterized by infrared, nmr and deuteration studies. In addition, an X-ray crystal structure analysis of one of these complexes, $IrH(CO)(NCCH{=}CHCN)(Ph_3P)_2$, has been reported.

These hydrido-olefin complexes are models of compounds which have often been cited as being unstable intermediates in many important homogeneously catalyzed reactions. The fact that the hydrido-olefin complexes reported herein are isolable, and that they do not undergo transformation to the alkyl complexes *via* hydride transfer as postulated in many catalytic reactions, might be attributed to at least two factors. The general kinetic inertness of iridium complexes compared to the analogous complexes of the lighter congeners is probably involved. The second factor is the presence of an activated olefin strongly bonded to the metal in the complex. The coordinated activated olefin could, by with-drawing sufficient electron density from the metal atom, strengthen the metal-hydrogen bond, and deter hydride transfer.

It is quite possible that the relative orientation of the olefin with respect to the hydride ligand is an important factor when hydride transfer is involved. In $IrH(CO)(NCCH{=}CHCN)(Ph_3P)_2$ the C=C axis of the olefin is perpendicular to the Ir-H axis. Further, nmr data suggest that the olefin is rigidly bonded in this complex. These

factors may be less conducive to hydride transfer to the olefin than in systems where the olefin is less tightly bound. Olefin rotation is known to occur in some complexes, and the C=C axis can sometimes become parallel to the M-H axis. Conceivably, parallel orientation may be the lowest energy barrier to hydride transfer. This situation may prevail in the reaction between acrylonitrile and the hydridoiridium complex. A σ-alkyl-π-olefin complex was obtained, but no hydrido-olefin complex was isolated from this reaction mixture. Hopefully, the study of further model compounds of intermediates in catalytic reactions will cast more light on the nature of these catalysts.

The activated olefin tetracyanoethylene has been found to form a novel product when it reacts with the hydridoiridium substrates. This σ-keteniminato-π-olefin complex is the first reported keteniminato-complex of a noble metal, and it may form *via* a 1,4-addition reaction. An X-ray crystal structure analysis has recently been described for this complex.

Acetylene reactions with the hydridoiridium substrates have been studied, and a variety of products have been obtained. The new compounds include those in which insertion of an acetylene into an Ir-H bond has occurred. Also, a terminal acetylene has been found to react with iridium (I) complexes *via* oxidative addition with the resultant formation of an acetylido-complex. Iridium complexes containing π-bonded acetylenes have also been prepared. The significance of some of these complexes as models for proposed intermediates in the catalytic polymerization of acetylenes has been discussed in the body of the dissertation.

REFERENCES

1. G. Wilkinson and J. M. Birmingham, J. Am. Chem. Soc., 77, 3421 (1955).
2. J. Chatt, Science, 160, 723 (1968).
3. P. E. Potter, L. Pratt, and G. Wilkinson, J. Chem. Soc., 524 (1964).
4. A. P. Ginsberg in "Transition Metal Chemistry", Vol. 1 (R. L. Carlin, ed.) Marcel Dekker, New York, 1965, p. 111.
5. M. G. Burnett, P. J. Connolly, and C. Kemball, J. Chem. Soc., (A), 800 (1967).
6. R. G. S. Banks and J. M. Pratt, Chem. Commun., 776 (1967).
7. M. L. H. Green and D. J. Jones, Adv. Inorg. Chem. Radiochem., 7, 115 (1965).
8. J. Chatt, Proc. Chem. Soc., 318 (1962).
9. J. Halpern, "Homogeneous Catalysis", Advances in Chemistry Series, No. 70, American Chemical Society, Washington, D. C., 1968.
10. R. F. Heck, "Mechanisms of Inorganic Reactions", Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.
11. R. F. Heck and D. S. Breslow, J. Am. Chem. Soc., 83, 4023 (1961).
12. S. D. Robinson and B. L. Shaw, Tetrahedron Letters, 20, 1301 (1964).
13. G. N. Schrauzer and K. C. Dewhirst, J. Am. Chem. Soc., 86, 3265 (1964).
14. H. C. Clark and W. S. Tsang, J. Am. Chem. Soc., 89, 529 (1967).

15. H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, J. Am. Chem. Soc., 89, 3360 (1967).

16. H. A. Tayim and J. C. Bailar, Jr., J. Am. Chem. Soc., 89, 3420, 4330 (1967).

17. H. Singer and G. Wilkinson, J. Chem. Soc. (A), 2516 (1968).

18. P. S. Hallman, B. R. McGarvey, and G. Wilkinson, J. Chem. Soc. (A), 3143 (1968).

19. P. Uguagliati and W. H. Baddley, J. Am. Chem. Soc., 90, 5446 (1968).

20. K. F. Watterson and G. Wilkinson, Chem. Ind. (London), 991 (1959).

21. W. H. Baddley and L. M. Venanzi, Inorg. Chem., 5, 33 (1966).

22. R. G. Guy and B. L. Shaw, Adv. Inorg. Chem. Radiochem., 4, 77 (1962).

23. W. H. Baddley, J. Am. Chem. Soc., 90, 3705 (1968).

24. J. F. Harrod, D. F. R. Gilson, and R. Charles, Can. J. Chem., 47, 2205 (1969).

25. J. P. Collman and W. R. Roper, Adv. Organometal. Chem., 7, 53 (1968).

26. B. Clarke, M. Green, F. G. A. Stone, J. Chem. Soc., (A), 951 (1970).

27. G. W. Parshall and F. N. Jones, J. Am. Chem. Soc., 87, 5356 (1965).

28. R. Cramer, J. Am. Chem. Soc., 86, 217 (1964).

29. L. Vaska, Accounts Chem. Res., 1, 335 (1968).

30. J. P. Collman, Accounts Chem. Res., 1, 136 (1968).

31. W. Beck, W. Hieber, and G. Neumair, Z. Anorg. Allg. Chem., 344, 285 (1966).

32. W. Beck, R. E. Nitzschmann, H. S. Smedal, J. Organometal. Chem., 8, 547 (1967).

33. S. R. Su, J. A. Hanna, and A. Wojcicki, J. Organometal. Chem., 21, P21 (1970).

34. W. P. Neuman and K. Kühlein, Tetrahedron Letters, 29, 3415 (1966).

35. W. P. Neuman, R. Sommer, and E. Müller, Angew. Chem. Internat. Ed., 5, 514,515 (1966).

36. E. W. Abel, J. P. Crow, J. N. Wingfield, Chem. Commun., 967 (1969).

37. G. N. Schrauzer, J. Am. Chem. Soc., 81, 5310 (1959).

38. A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 89, 5989 (1967).

39. K. C. Dewhirst, Inorg. Chem., 5, 319 (1966).

40. R. Cramer, Accounts Chem. Res., 1, 186 (1968).

41. B. L. Booth and R. G. Hargreaves, J. Chem. Soc. (A), 2766 (1969).

42. L. Vaska, Inorg. Nucl. Chem. Letters, 1, 89 (1965).

43. L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerley, J. Org. Chem., 27, 3930 (1962).

44. J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes", Elsevier, New York, 1968, p. 265.

45. J. P. Collman and J. W. Kang, J. Am. Chem. Soc., 89, 844 (1967).

46. Y. Okamoto, A. Gordon, F. Movsovicius, H. Hellman, and W. Brenner, Chem. Ind. (London), 2004 (1961).

47. A. Furlani, I. Collamati, and G. Sartori, J. Organometal. Chem., 17, 463 (1969).

48. J. Chatt, L. A. Duncanson, and R. G. Guy, Chem. Ind. (London), 430, (1959).

49. J. O. Glanville, J. M. Stewart, and S. O. Grim, J. Organometal. Chem., 7, P9 (1967).

50. K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, Inc., San Francisco, 1962, p. 28.

51. S. S. Bath and L. Vaska, J. Am. Chem. Soc., 85, 3500 (1963).

52. S. J. LaPlaca and J. A. Ibers, J. Am. Chem. Soc., 85, 3501 (1963).

53. C. O'Connor and G. Wilkinson, J. Chem. Soc., (A), 2665 (1968).

54. M. Ciechanowicz, A. C. Skapski, and P. G. H. Troughton, Acta Cryst. A25 (Supplement) S172 (1969).

55. G. Yagupsky and G. Wilkinson, J. Chem. Soc. (A), 725 (1969).

56. L. Vaska, J. Am. Chem. Soc., 88, 4100 (1966).

57. L. Vaska, Chem. Commun., 614 (1966).

58. P. S. Braterman, R. W. Harrill, and H. D. Kaesz, J. Am. Chem. Soc., 89, 2851 (1967).

59. E. W. Tillay, Ph.D. Dissertation, Louisiana State University, 1967.

60. L. Malatesta, G. Caglio, and M. Angoletta, J. Chem. Soc., 6974 (1965).

61. J. F. Harrod, D. F. R. Gilson, and R. Charles, Can. J. Chem., 47, 1431 (1969).

62. F. Canziani, U. Sartorelli, and F. Zingales, Chem. Ind. (Milan), 49, 469 (1967).

63. J. P. Collman, F. D. Vastine, and W. R. Roper, J. Am. Chem. Soc., 90, 2282 (1968).

64. J. S. Ricci, J. A. Ibers, M. S. Fraser, and W. H. Baddley, J. Am. Chem. Soc., 92, 3489 (1970).

65. K. W. Muir and J. A. Ibers, J. Organometal. Chem., 18, 175 (1969).

66. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965, p.99.

67. G. Schrumpf and W. Lüttke, Tetrahedron Letters, 31, 2635 (1969).

68. V. S. Watts, J. H. Goldstein, J. Chem. Phys., 46, 4165 (1967).

69. J. Halper, W. D. Closson, and H. B. Gray, Theor. Chim. Acta, 4, 174 (1966).

70. D. Evans, J. A. Osborn, and G. Wilkinson, J. Chem. Soc. (A), 3133 (1968).

71. C. K. Brown, and G. Wilkinson, Chem. Commun., 70 (1971).

VITA

Margaret Shirley Fraser is a native of Biggar, Saskatchewan, Canada where she received her elementary education. She completed her high school at Edmonton, Alberta and entered the University of Alberta, situated there. She received a B.S. in Honors Chemistry in 1948 and an M.S. in Biochemistry in 1950. After a year as Research Assistant she emmigrated to the United States where she was employed as a Project Assistant at McArdle Laboratories for Cancer Research, Madison, Wisconsin. In 1952 she became an instructor with the University of Wisconsin Center System (now University of Wisconsin - Parkside) at Racine, Wisconsin.

During the summer of 1965, Miss Fraser became a graduate student at Louisiana State University and during 1969-1970 she was on leave of absence from her teaching post to work full-time on the Ph.D. degree. She will return to teaching in Racine at the conclusion of her degree.

EXAMINATION AND THESIS REPORT

Candidate: Margaret Shirley Fraser

Major Field: Chemistry

Title of Thesis: Reactions of Activated Olefins and Acetylenes with Hydridoiridium Complexes

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

June 18, 1971